

THE MICROSCOPICAL EXAMINATION

OF THE

ALLOYS OF COPPER AND TIN.

By

WILLIAM CAMPBELL.

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY IN THE FACULTY OF APPLIED SCIENCE OF
COLUMBIA UNIVERSITY.

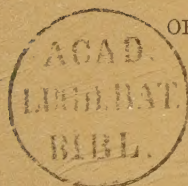
MAY, 1903

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ALLOYS OF COPPER AND TIN.

(BEING AN APPENDIX TO THE REPORTS OF THE
ALLOYS RESEARCH COMMITTEE.)

BY

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EXCERPT MINUTES OF PROCEEDINGS
OF THE MEETING
OF
THE INSTITUTION OF MECHANICAL ENGINEERS,
IN LONDON, 20TH DECEMBER 1901.

WILLIAM H. MAW, ESQ., PRESIDENT,
IN THE CHAIR.

PUBLISHED BY THE INSTITUTION,
STOREY'S GATE, ST. JAMES'S PARK, WESTMINSTER, S.W.

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THE MICROSCOPICAL EXAMINATION OF THE ALLOYS OF COPPER AND TIN.

(Being an Appendix to the Reports of the Alloys Research Committee.)

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The following research was made in the metallurgical laboratory of the Royal School of Mines, London, with a view to explain the complete freezing-point curve of the copper-tin alloys published in the Fourth Report of the Alloys Research Committee,* and to note the change of structure due to casting.

The microstructure of the copper-tin alloys has been studied by Behrens, Charpy, Stead, and others. Behrens divides these bronzes into two principal groups: bronzes rich in copper, containing from 1 to 25 per cent. of tin, and bronzes rich in tin containing over 25 per cent. of tin. With the exception of the metals for mirrors (25 to 35 per cent. of tin) which appear homogeneous, Behrens says that in all bronzes a portion richer in copper or richer in tin may be detected, forming the fundamental mass, the former in alloys rich in copper, the latter in those rich in tin.†

Charpy divides them into those rich in copper, containing 100 to 73 per cent. of copper; and those rich in tin, which latter are again subdivided into four groups: 0 to 3 per cent. of copper, in which tin crystallizes in the matrix; 3 to 55 per cent. of copper, in which a compound of tin and copper crystallizes out of the matrix; 55 to 65 per cent. of copper, which have a structure quite homogeneous

* For First, Second, Third, Fourth, and Fifth Reports, see Proceedings 1891, page 543; 1893, page 102; 1895, page 238; 1897 page 31; and 1899, page 35.

† Metallographist. Vol. i., page 193.

and difficult to resolve; and 65 to 73 per cent. of copper, in which hard white grains crystallize in the higher eutectic.

The curve of fusibility, as determined by Le Chatelier, is composed of three branches, forming by their intersections two points which correspond with alloys containing 3 and 72 per cent. of copper.

0 to	3 per cent. of copper:	straight:	fall.
3 „	72 „	„	uniformly curved: rise.
75 „	100 „	„	almost straight: rise.

The meaning of the curve is seen to be as follows. Alloys containing 0 to 3 per cent. of copper consist of tin and of tin crystallizing in more and more eutectic. At the point where the two branches meet occurs the first or lower eutectic. Above this point, bright slender porphyritic crystals form, and their number increases till at 61·8 per cent. they form a uniform mass, probably a definite compound Sn Cu_3 . At 68·28 per cent. of copper the alloy is again found to be homogeneous,* and is probably another definite compound Sn Cu_4 . Between these two points, the alloys seem to consist of Sn Cu_3 and Sn Cu_4 , separately solidified, the latter in the former. From 68·28 per cent. of copper to 72 per cent. we pass from the compound Sn Cu_4 to the second eutectic. Above 72 per cent. the copper crystallizes out in the eutectic as yellow dendrites, and then as skeleton crystals, which increase in number and size until at 100 per cent. they occupy the whole mass.

If, however, we study the complete cooling curve of the Copper-Tin Alloys,† by Sir William Roberts-Austen, reproduced in Fig. 1 (page 1214), it is seen that the meaning of only a part of the curve has been explained above. The branches *c*, *e*, and *f* remain unaccounted for.

The result of the microscopical study of these alloys is shortly as follows:—

* Roberts-Austen. An Introduction to the Study of Metallurgy, page 99; Laurie. Journal of the Chemical Society, Transactions, vol. liii, 1888, page 104.

† An Introduction to the Study of Metallurgy, page 70; Fourth Report of the Alloys Research Committee, Proceedings 1897.

When 1 per cent. of copper is present, the first eutectic alloy is obtained, that is, the one with the lowest freezing-point; and between pure tin on the one hand, and this alloy containing 1 per cent. of copper on the other, tin is found crystallizing in the eutectic, first in grains, then in dendrites.

When the percentage of copper is increased above 1 per cent., thin bright needles are seen, which increase in size and number, and vary in their method of grouping, until 8 per cent. of copper is reached. According to Stead, their composition also varies, increasing in copper (from Cu Sn) as the total percentage of copper in the alloy increases.*

A third constituent is seen when the copper exceeds 8 per cent. We have the eutectic or ground-mass enclosing the bright porphyritic crystals, but these bright crystals are seen in places to have grown on and around a different kind of crystal, which is easily distinguished from the rest because it turns black when exposed to the air for any length of time. It is not a case of one crystal varying in composition from the centre to the faces; for a sharp line of junction can be seen between the two constituents. As the percentage of copper is increased, the more easily oxidized central crystals increase in number and size, whereas the bright outer crystals begin to diminish together with the eutectic. Therefore it would appear that in alloys containing more than 8 per cent. of copper the first constituent to crystallize out is the easily oxidized central crystals. This causes the first halt in the cooling curve *a b*. Then the bright crystals solidify, causing the second halt, on the branch *f*. Lastly the eutectic solidifies, and the third halt is reached, on the branch *g*. As branch *f* is horizontal, it would seem that the bright crystals have a definite composition when above 8 per cent. of copper is present in the alloy; but when the branch *f* joins the outer curve *b a*, and falls to *b*, these crystals no longer have a definite composition, and their percentage of copper falls. The following is the analysis of the crystals, which agrees very nearly with that given by Stead:—

* Journal, Society of Chemical Industry, June 1897, page 506.

FIG. 1.—Freezing-point Curves of Copper-Tin Alloys, reproduced from Plate 10 of Fourth Report, 1897.

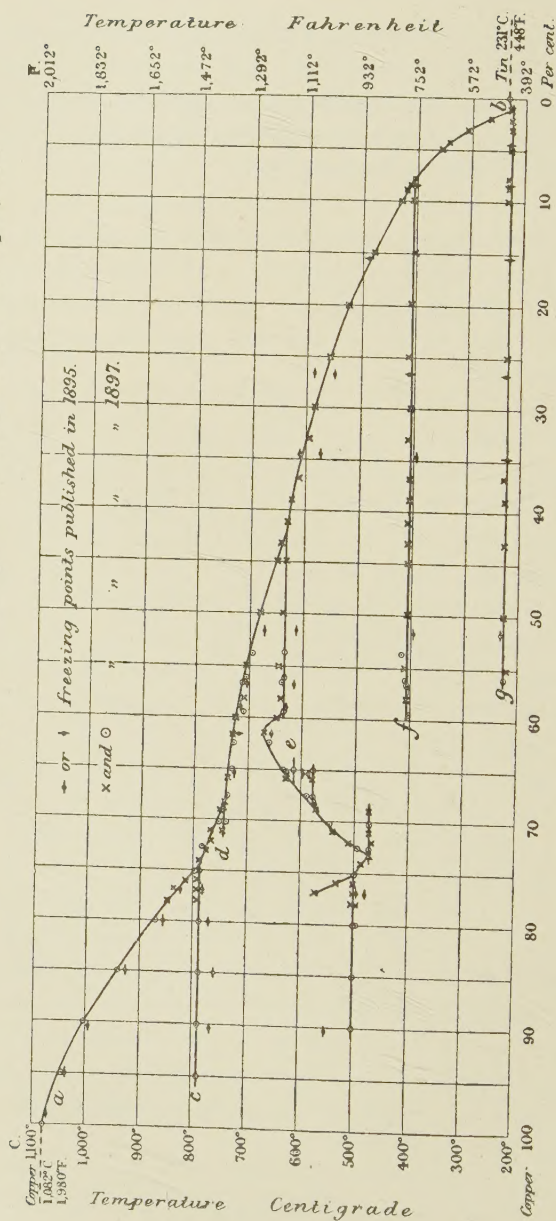
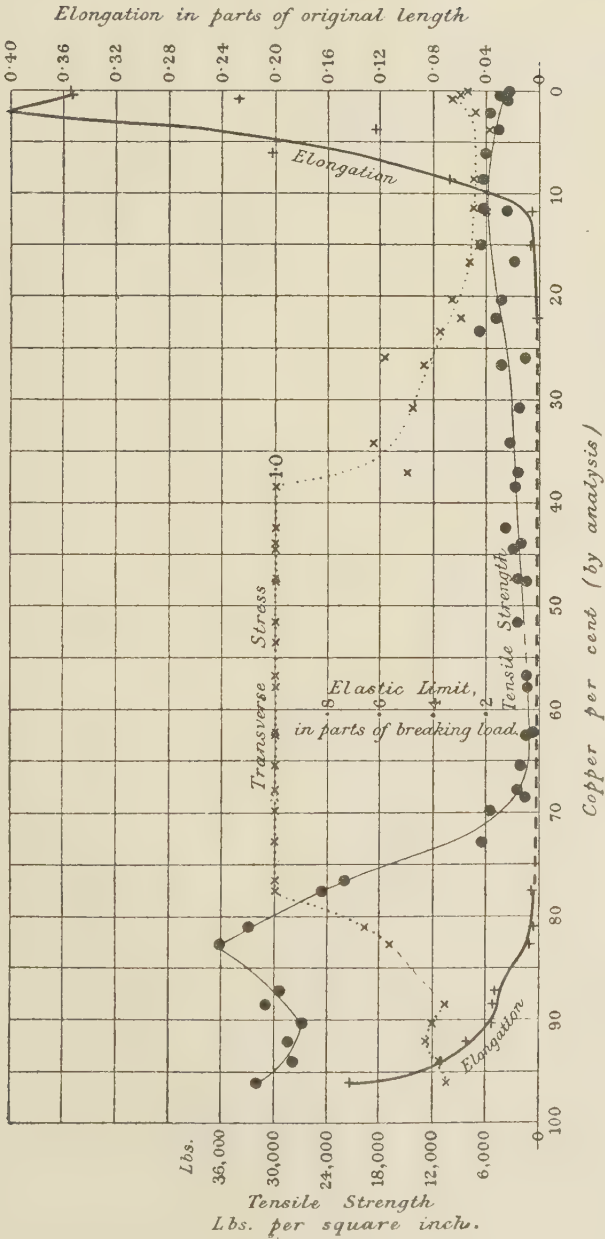
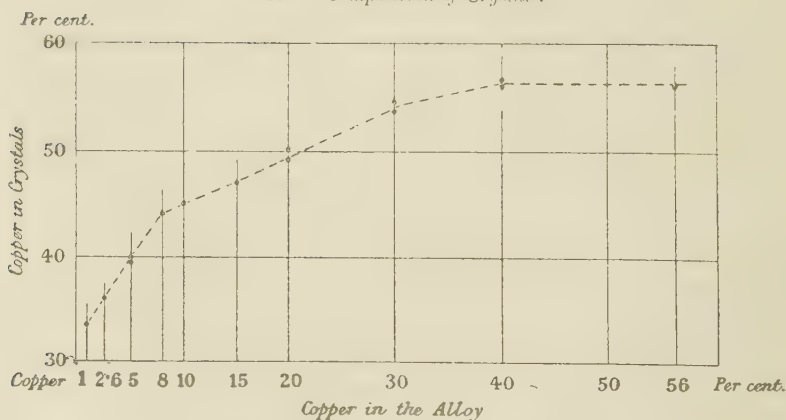


FIG. 1A.—*Tensile Strength, Elongation, and Transverse Stress of Copper-Tin Alloys.*
(Plotted from "Alloys Brasses and Bronzes," Thurston, Part 3, Table LXV., pages 342-3.)



Alloy contained	Per cent.	copper, crystals contained	Per cent.
	1	33.5 copper.	
"	2.6	"	36
"	5	"	{ 40
"	8	"	{ 39.5
"	10	"	44
"	15	"	45
"	20	"	47.2
"	30	"	{ 49.2
"	40	"	{ 50.2
"		"	{ 53.5
"		"	{ 54.5
"		"	{ 56
"		"	{ 56.5

FIG. 2.—Composition of Crystals.



The variation of 1 per cent. in several of the analyses is due to the difficulty in getting rid of any oxide of tin, entangled amongst the crystals, without dissolving out any of the constituents of the crystals.

If a curve be plotted showing the relation between the percentage of copper in the alloy and the percentage of copper in the crystals, a straight line is obtained from 1 to 8 per cent. of copper in the alloy, but at 10 per cent. the crystals are quite away from this line, Fig. 2.

With 41 per cent. of copper in the alloy, there is a distinct change in the character of the alloy, Fig. 1 (page 1214). The addition of 1 per cent. of copper has changed the composite crystals from large plate-like masses to small lath-like rods, surrounded as before by the bright constituent. As the percentage of copper in the alloy increases, the eutectic diminishes, and at 56 per cent. disappears*: the central and more easily oxidizable portion of the composite crystals steadily increases, and the bright constituent decreases, until 61·7 per cent. of copper is reached, when the whole mass appears to be uniform. This is the alloy Sn Cu_3 .

From 61·7 to 68·28 per cent. of copper, Fig. 1, the higher compound Sn Cu_4 crystallizes out round or alongside of decreasing proportions of Sn Cu_3 , till at 68·28 per cent. the alloy is uniform throughout, and is probably another definite compound. The difference between these two compounds is very marked; that containing the 68·28 per cent. of copper is harder, of lighter colour, and less easily attacked by acids. It is extremely brittle, and when quenched it flies to pieces. It is remarkable for the high degree of polish which it takes. The lower compound Sn Cu_3 on the other hand has a marked cleavage.

From 68·28 to 74 per cent. of copper, where the second eutectic of the series occurs, Fig. 1, the alloys are seen to consist of the bright Sn Cu_4 surrounded by eutectic. They are generally granular, and the borders of each grain or crystal consist of bright Sn Cu_4 , while the centre is occupied by Sn Cu_4 as dendrites or grains set in the eutectic. The amount of the eutectic increases with the increase of copper, until it occupies the whole mass.

The part of the curve of solidification, *b a*, is seen to be a continuous rise from 68·3 to 74 per cent. Cu, and the 74 per cent. alloy has a higher freezing-point than Sn Cu_4 . Hence if 74 per cent. be a eutectic, it must have formed when the alloy was solid. The third branch *c* of the complete cooling curve resembles an ordinary cooling curve having two branches inclined to each other and a horizontal branch at their intersection, which occurs at about

* Stead. Journal, Society of Chemical Industry, June 1897, page 506.

74 per cent. Seeing that this branch *e* passes through the series from 90 to 41 per cent. of copper, it appears probable that at 41 per cent. the change in the alloy is simply one of arrangement. Since the alloys with 68.28 and 61.7 per cent. of copper, though seemingly compounds, have at least two distinct breaks in their cooling curves, it would appear that branch *e* in part, if not wholly, represents a rearrangement after solidification, and resembles the lower curve (Ar_1) for the carbon-irons.* So it would seem that in this division of the series the alloys solidify as a whole at the upper break in their cooling curve; but that, when they cool down, a re-arrangement takes place, and the formation of dendrites of $Sn Cu_4$ is obtained in the second eutectic. The eutectic alloy solidifies as a whole at about 780° C. (1,440° F.), but at 480° C. (896° F.) its structure changes to that of a eutectic.

In the discussion following the admirable Paper† on the Quenching of Copper-Tin Alloys, by Messrs. Heycock and Neville, at the Royal Society, it was pointed out that the present author had attempted to settle this question by quenching (in cold water) several of the furnace-cooled alloys which had been reheated to 700° C. (1,290° F.) This temperature proved to be below the melting point of each of the alloys so treated. The 73 per cent. alloy was first examined. It was found that the original structure had been entirely destroyed in the treatment, and the new structure was very similar to that of the alloy when cast. That is to say, the bright dendrites and veins in the eutectic are only distinguished under some 300 diameters magnification. The 71 per cent. alloy gave the same result, only more marked. When the 68.3 per cent. alloy was thus treated, it became so brittle and strained that on standing it broke up into fragments. On etching and examining the fragments, the original structure was missing. The 66 per cent. alloy also gave the appearance of having been cast. No trace could be seen of anything like a eutectic such as had been observed in the original alloy. On quenching the 61 per cent. alloy it broke up, though not to the extent

* Stansfield. Present Position of Solution Theory: Journal, Iron and Steel Institute, 1899, Part II, page 169; also Proceedings 1899, Plate 5.

† Proceedings, Royal Society, vol. lxxviii, page 171.

of that containing 68·3 per cent. of copper. The large crystallization characteristic of the original alloy was destroyed. This method of treatment could not be used below 61 per cent. of copper because, when the tin rises above 40 per cent., the bright constituent, which solidifies out about 400° C. (720° F.), comes in, and therefore re-heating to anything like 650° C. (1,170° F.) would melt part of the alloy.

From the above it is seen that, between 74 and 60 per cent., re-heating the furnace-cooled alloys to 700° C. (1,290° F.) does not melt any portion of them, and that quenching at that temperature causes a new structure, which, in each case under examination, was similar to that due to casting.

It was naturally concluded that, if these quenched alloys were annealed at about 700° C. (1,290° F.) and slowly cooled, the effects of quenching would be obliterated, and the normal structure would be restored. The 73 per cent. Cu alloy which had been quenched was placed in a porcelain cup, covered with powdered charcoal to prevent oxidation, and annealed in a muffle for a short time. The muffle was then allowed to cool, and the alloy examined. The change was incomplete, part of the alloy being in a transition state. In all parts the effects of quenching had disappeared, and in several places the normal structure had been quite restored, and the usual bright dendrites were seen in the eutectic. This transition state showed clearly how the change had taken place. Large bright grains separated from each other by a darker material (the eutectic) were seen, and gave the alloy the appearance of a decomposing rock. In places these bright grains were splitting up into dendrites and eutectic: so that the whole series of structures, from that of the bright granular material on the one hand to that of the normal dendrites on the other, could be clearly followed. Hence it seems that the true explanation of the branch *c*, between 68·28 and 61·7 per cent. of copper is that it is one of re-arrangement in the solid.

When the copper is increased above 75 per cent., the colour of the alloy changes sharply from a bluish tint to a distinct yellow. A new constituent appears, consisting of rounded yellow grains. This has crystallized out first, and then a bright white substance has formed round the yellow grains and in the eutectic. It seemed probable

that at about 790°C. ($1,454^{\circ}\text{F.}$) the mass solidified entirely round the yellow grains, and that at a lower temperature it re-arranged itself into bright grains and eutectic. To test this point a 76 per cent. furnace-cooled alloy was re-heated to about 700°C. (1290°F.) and quenched. No sign of melting was noticed. On examination the grains of copper were found to be unaltered, but the structure of the eutectic and the bright grains had completely disappeared. The eutectic appeared to be in the form of large grains, in which the bright constituent had solidified like a 73 per cent. alloy. Therefore it may be assumed that branch *c* represents a solidification of the whole mass, and *e* a re-arrangement in the solid.

With the increase of the total copper in the alloy, the yellow grains increase, forming dendritic skeletons, and altering in colour from yellow to red as pure copper approaches. The change of colour is due to the fact that the dendritic copper contains some tin in solution, which gradually disappears, and hence the colour changes from yellow to red. For the same reason the temperature of solidification of the copper dendrites increases. The same thing occurs in the Copper-Antimony Alloys.*

Between 90 and 95 per cent. the eutectic disappears, and between 95 and 100 per cent. the bright borders merge into the dendrites of copper.

Hence from 75 to 100 per cent. of copper the outer curve from *c* to *a* represents the solidification of the yellow dendrites and grains, which at first contain some tin but finally become pure copper. The horizontal branch *c* denotes the solidification of the remainder, which, when between 75 and 90 per cent. Cu is present in the alloy, re-arranges itself into a bright constituent in the form of grains and borders surrounding the yellow dendrites, and into eutectic; and this change is marked by *e* in the cooling curve.

Change in Structure due to Casting.—When the alloys which contain between 0 and 1 per cent. Cu are cast, the tin crystallizes out as grains very much smaller than those of the slowly-cooled alloys. The proportion which the grains bear to the eutectic is

* Stead. Journal, Society of Chemical Industry, December 1898, page 1111.

greatly increased by casting ; and this seems to point to the fact that in cooling quickly the grains of tin retain some copper. On the other hand, no crystals can be seen in the 1 per cent. alloy when cast, whereas when it is slowly cooled in the furnace they are present. Thus the eutectic contains slightly more copper when cast than when slowly cooled.

When from 1 to 8 per cent. of copper is present, casting produces a fine network of bright crystallites throughout the eutectic. On treatment with 10 per cent. nitric acid and washing with dilute hydrochloric, the eutectic is dissolved, and a fine dark brown powder is left behind, which seems to be composed of very small shapeless plates. The crystallites form well-defined skeleton crystals, of which the component parts thicken with the increase in copper. The 10 per cent. alloy shows no sign of a third constituent, although, when a 9 per cent. alloy was cast in a pasty condition, the third constituent could be clearly seen, forming the core of some of the bright crystals. In this case many of the bright crystals possessed their characteristic form.

The 20 per cent. Cu alloy is composed of bright rod-like crystals, which, under a magnification of some 300 diameters, are seen to be composed of two constituents, as in the slowly-cooled alloy. These rods increase in size as the copper is increased to 40 per cent. The various residues, after treatment with dilute nitric acid, become more and more coherent, until at 40 per cent. a spongy skeleton is left behind. With 41 per cent. of copper the crystals change in character, and become more or less fibrous in appearance, whilst beautiful structures are seen on the surface of the alloy. But little eutectic can be seen ; and when the copper is increased to about 50 per cent. no eutectic can be distinguished, the alloy being apparently composed of the bright and dark constituents only. The bright surrounds the dark as a matrix. As the copper in the alloy is increased, the bright constituent diminishes and finally disappears at about 61 per cent.

Between 62 and 68 per cent. Cu the alloys present a striking appearance when cast. They consist of the bright constituent, probably Sn Cu_4 , intersected by veins and parallel lenticular bands of the dark material. There is no trace of the eutectic-like

structure. When the alloy is near 61·7 per cent. Cu in composition, there is naturally but little of the bright constituent, which surrounds the grains of the dark material like an envelope. The appearance is similar to that of the alloy when slowly cooled, but more minute. It would seem probable that, if the cooling could be performed with sufficient rapidity, the resultant alloys (between 62 and 68 per cent.) would give a series, in which each consisted of a single constituent: that the character of the series would vary from that of Sn Cu_3 to Sn Cu_4 quite uniformly. In other words, the separation into two constituents would be prevented. The 68 per cent. alloy when cast appears to consist of polygonal grains of varying size and with bright borders. When deeply etched, and examined under a magnification of some 2,000 diameters, the grains are seen to be composed of systems of bright and dark parallel laminae, the whole closely resembling a eutectic. Amongst some of the bright laminae or dendrites there is a distinct tendency to form skeleton crystals, whose form is quite distinct from those seen in the slowly-cooled alloy.

Between 68·28 and 74 per cent. of copper the structure is granular, the mass being made up of polygonal grains. Two constituents can be seen, one bright, the other dark. The bright forms round the edges of the grains, and appears like radiating lines. Under high magnification bright grains and dendrites can be seen in the dark constituent, which is the eutectic. The 74 per cent. alloy is made up of grains, each of which has a particular orientation, thus giving the alloy a speckled appearance. Only under very high powers can its eutectic nature be discovered.

At about 76 per cent. Cu the copper dendrites and grains make their appearance. They are very minute, and it is hard to distinguish between them and the bright constituent which surrounds them.

In the 80 per cent. Cu alloy the dark dendritic crystals of copper can clearly be seen, forming parallel groups. It is quite clear, by comparing the proportion of copper dendrites and grains in alloys of the same composition—the one cast, the other slowly cooled—that the dendrites in the cast alloy must contain more tin than in the slowly cooled. Charpy points out that in quickly-cooled alloys the eutectic may even disappear, notwithstanding

the presence of some 7 to 8 per cent. of tin; and he considers the bright borders and grains to be part of the eutectic. The effect of oxidation, when this occurs, shows that the dendrites vary in composition from centre to border. The surface structure of the alloys between 80 and 100 per cent. Cu is often very fine, and generally consists of numbers of distinct skeleton crystals, which stand out prominently above the surface.

The result of casting, therefore, is always to make the structure comparatively minute. In alloys rich in copper, the dendrites of copper contain more tin when cast than when slowly cooled. Similarly in those alloys containing dendrites of tin, the tin probably tends to retain more copper when cast. Again, casting tends to raise the percentage of copper in the first eutectic, and probably also in the second. Lastly, it seems that Sn Cu₄ when cast has a different crystalline form from that which it possesses when slowly cooled.

During January 1901 a recording pyrometer was set up in the Metallurgical Department of the Royal School of Mines, and this offered a means of verifying the results obtained by annealing. The pyrometer was first made to give the cooling curve of the particular alloy under treatment, after which the alloy was quenched at different temperatures, corresponding with particular points on its cooling curve. Sections were made from the quenched alloys, and examined in the usual way.

A description of the pyrometer is hardly necessary here, but Plate 189 shows a front and back view and the pyrometer in place. In Fig. 5 the recorder* is seen on the left-hand side, whilst the galvanometer circuit is seen on the right. The galvanometer is a "dead-beat," and stands on a shelf let into the angle of the wall, thus making it quite rigid. The beam of light emerges from a slit in the casing of an incandescent electric light, fixed at the side of the recorder; by means of a single lens it is focussed upon the mirror of the galvanometer, whence it is reflected back to the slit and scale of the recorder. Both galvanometer connections pass to the cold junction of the thermo-couple, one direct,

* Designed by Dr. A. Stansfield.

the other by way of a post-office resistance-box. The cold junction is seen on the upper shelf on the right, and from it proceed the wires of the thermo-couple. By means of the resistance box the temperature readings of the scale on the recorder can be varied at will.*

The alloy was melted in a small crucible, placed inside a larger. The inter-space was filled with asbestos fibre, and in this way slow cooling was obtained. The average time of fall from $1,000^{\circ}\text{C.}$ to 500°C. ($1,800^{\circ}\text{F.}$ to 900°F.) was half-an-hour, which was found to be a sufficiently slow rate to admit of the alloy being quenched exactly at the right temperature. When liquid, the alloy was removed from the fire, together with outer crucible and lid, and placed upon two bricks on the table. The thermo-couple, covered with its clay case and mica insulation, was then pushed through a hole in the lid into the molten metal. It was soon found that, if the thermo-couple was not kept well down in the alloy, the readings obtained were too low. When the spot of light on the scale reached the desired temperature, the wires of the thermo-couple were quickly withdrawn from the clay tube, and the inner crucible and alloy were plunged into cold water. Each of the alloys treated was quenched both when in the liquid state and also at the moment of complete solidification; this point is never less than 685°C. (1265°F.) in alloys containing more than 61 per cent. Cu.

The following results were obtained:—

50 per cent. Cu, 50 per cent. Sn. The cooling curve showed four breaks, namely 680° , 635° , 410° , and 225°C. ($1,256^{\circ}$, $1,175^{\circ}$, 770° , and 437°F.)

As the last two have been explained, they were not taken into consideration.

When quenched liquid, the alloy had a granular appearance. The grains were small, and were enveloped in a darker material, probably the eutectic. Etching failed to bring out any structure in the grains themselves.

Quenched at 650°C. ($1,202^{\circ}\text{F.}$), which is below break 1, the alloy showed a granular appearance, much larger than the above. The dark

* Proceedings 1891, page 546.

enveloping matrix had increased in quantity, and the grains showed a tendency to form dendrites. Besides the large grains and matrix, patches of very fine grains were seen on etching the specimen. It is possible that they represent the bright constituent which crystallizes out in the 1 up to 8 per cent. alloys.

When quenched below break 2, at 600° C. ($1,112^{\circ}$ F.), the structure was found to have changed considerably. Although more or less granular in parts, the grains appeared to be crystals cut across their main axis. The alloy was distinctly crystalline in the hand-specimen, and under the microscope each crystal was seen to be composed of numbers of parallel squat laths. These could not be distinguished into two constituents, as in the case of the slowly-cooled alloy; but their form closely resembles that in the slow-cooled specimen.

66 per cent. Cu, 34 per cent. Sn. Three breaks at 740° , 635° , and 580° C. ($1,364^{\circ}$, $1,175^{\circ}$, and $1,076^{\circ}$ F.)

The appearance of the alloy which has been quenched when liquid is the same as that of the alloy quenched at its solidification point, but much more minute. Quenched on solidification, the alloy presents a remarkable appearance. It has a cell-like structure, the centre of each cell being dark and the walls light coloured; many of the cells appear to have a white nucleus. In parts of the field dark lines are seen, short as yet, but the beginning of a new structure. The whole presents the appearance of the solidification of two liquids which will not mix together.

If the alloy is quenched before the end of the first break, though after the solidification of the whole mass, a new structure is seen. The cells remain with their white walls; but the background has become split up into dark and light, like a mesh. Between one system of mesh and the adjoining there is an irregular dark band.

Quenched below break 1, at 700° C. ($1,292^{\circ}$ F.), the cell structure disappears, and the whole field is covered with a "shot" structure, closely resembling the "schiller" structure of bronzite in appearance. The alloy is crystalline, each crystal having a different orientation and appearance. If the alloy is cast on an iron

plate the "shot" structure reaches its full development; but it is absent in an ingot of the alloy, in which a coarse banded structure takes its place.

When the alloy is quenched below break 2, at 610° C. ($1,130^{\circ}$ F.), the "shot" structure has almost entirely disappeared, and the alloy has the appearance of being slowly cooled, but with the difference that no eutectic-like structure can be discovered.

68.3 per cent. Cu, 31.7 per cent. Sn. Two breaks, 745° and 580° C. ($1,373^{\circ}$ and $1,076^{\circ}$ F.)

When this alloy was quenched liquid, the author failed to obtain any structure on etching. Quenched on solidification, the alloy shows a remarkable structure. Black grains and dendrites can be seen without the aid of a lens, and under the microscope dark grains are seen set in a lighter matrix; under a higher power the majority of these dendrites are seen to pass into the lighter matrix quite imperceptibly, the whole being covered by a fine needle-like structure. The whole appearance is one of incomplete metamorphosis. When quenched much below break 1, the dark grains disappear and the alloy appears homogeneous. If the alloy be cast on an iron plate, the structure is almost the same as that of the ingot, but is much smaller and more distinctly granular. The borders of each grain are rectilinear and sharply defined; orientation is marked.

73 per cent. Cu, 27 per cent. Sn. Four breaks 770° , 745° , 510° , 470° C. ($1,418^{\circ}$, $1,373^{\circ}$, 950° , 878° F.)

Quenched liquid, the structure is but imperfectly seen, and appears to consist of dark grains in a matrix. The alloy appears the same when quenched on solidification or between the first and second breaks at 760° C. ($1,400^{\circ}$ F.). It consists of dark dendrites and skeleton crystals in a lighter matrix. These dendrites have dark borders. The skeleton crystals appear to be the same as those whose pseudomorphs are seen on the surfaces of the slowly-cooled alloys.

Quenching at 650° C. ($1,202^{\circ}$ F.), below break 2, gives the alloy a mottled appearance. The dendrites have quite disappeared, and white irregular roundish patches are seen in the dark background. Throughout the whole mass minute rosette-like crystals of whitish colour are scattered. They are doubtless stunted forms of those which appear when the alloy is quenched at 500° C. (932° F.), below break 3. In this alloy large grains are seen with polygonal boundaries of a white material. The grains themselves are made up of white radiating crystals and bunches of granules. The matrix is black, but under high powers no eutectic can be made out. But for the latter peculiarity, the alloy is identical with the furnace-cooled specimen. The cast specimen shows traces of the skeleton crystals which form on the surface of the slowly-cooled alloys.

76 per cent. Cu, 24 per cent. Sn.

As the last two distinct breaks of this alloy are the same as those of the next alloy, quenching was performed only at solidification. Small yellow dendrites and skeleton crystals are seen set in a matrix which is markedly composite, the two constituents being dark minute rounded grains in a lighter matrix. No trace can be seen of the thick skeleton crystals found on the surface of the slowly-cooled alloy. Strange to say these appear quite distinctly when the furnace-cooled specimen is re-heated to about 750° C. ($1,382^{\circ}$ F.) and quenched. If re-heated to a pasty consistency and then quenched, the alloy seems to consist of these thick skeletons, in the midst of which appear the small yellow grains and dendrites.

80 per cent. Cu, 20 per cent. Sn. Three breaks, 870° , 790° , 500° C.
($1,600^{\circ}$, $1,454^{\circ}$, 932° F.)

When quenched from the liquid state, small yellow composite grains are seen in the dark structureless matrix. Quenching below break 1 produces large skeleton crystals composed of many-shaped yellow grains. No marked structure can be seen in the ground-mass. When quenched below break 2, at 750° C. ($1,382^{\circ}$ F.), the yellow grains have grown considerably, and the ground-mass has

a coarse fibrous appearance, which is quite distinct from that of the furnace-cooled alloy. Again, when the alloy is etched so as to make the dendrites of copper appear a blackish-red, they appear to be surrounded by a white envelope. In places the matrix appears quite amorphous.

From the above evidence it is clear that branch *e* of the cooling curve, Fig. 1, denotes a change of structure, and this is a change in the solid. In the 66 per cent. Cu alloy the first break is that of solidification; the second is that of separation into the light and dark constituents; whilst the third is that of the formation of the small eutectic out of a part of the light constituent. With regard to the 73 per cent. Cu alloy, it is doubtful whether the first break means the solidification of the whole or of only a part. If the latter, the second break *d* must mean the solidification of the remainder. It seems more probably to be one of change in the solid. The upper break of 76 per cent. Cu and 80 per cent. Cu alloys is that of the solidification of the copper grains and dendrites. The second means the solidification of the ground-mass (branch *c*). The horizontal part of *e* is the eutectic break; and therefore the third and doubtful break in the 76 per cent. alloy must mean the separation of the bright white constituent from the ground-mass, which is distinctly shown in Fig. 85, Plate 199.

Considering the many and distinctly different structures produced in the series by quenching at different temperatures, and by re-heating and then quenching, it is quite evident that the changes which take place during the cooling of an alloy of copper and tin, especially in the neighbourhood of the second eutectic alloy, are even more numerous than those of the Carbon-Irons.*

Preparation of the Alloys.—1. *Slowly cooled.*—Each alloy weighed 200 grains. In the alloys containing up to 1 per cent. of copper, the tin was first melted under potassium cyanide in a small clay crucible, and copper was then added in the form of foil (electro-copper containing 99·8 per cent. Cu). It was found

* Roberts-Austen. *Molecular Unrest in Solids*: Philosophical Society of Glasgow, 1900.

that the copper quickly dissolved in the tin. A large amount of the alloy containing 40 per cent. Cu and 60 per cent. Sn was carefully prepared by melting the copper first and then adding the tin. From this the alloys between 1 and 40 per cent. Cu were prepared by adding the requisite amount of tin. In each case the alloy was melted first, under potassium cyanide and carbonate, and the tin was added afterwards. In the alloys containing above 40 per cent. Cu the copper was melted and then the tin added. The crucible was well shaken in order to mix the contents thoroughly, and was then taken out of the fire and allowed to cool slowly on the top of the furnace in the open air. When cool the cyanide was washed away, and the button of alloy taken out.

2. *Cast*.—When the alloys were cast, a thick iron mould was used cold. The alloy was melted as before, and when liquid was poured into the mould. The resulting ingot was about $\frac{1}{4}$ inch thick. When the alloy contained only a small percentage of copper, the greater portion of the cyanide was first poured off, because it was found that it retarded the cooling when poured into the mould along with the alloy.

3. *Furnace-cooled*.—Each alloy weighed about 800 grains, and was prepared as before. When the alloy was thoroughly melted, the crucible and contents were placed in a hot larger crucible containing charcoal powder; this outer crucible was already in place in a hot fire. The lid was put on the crucible, and the fire was then banked up with ashes; the dampers were closed, and all draught stopped. In 24 to 36 hours the fire had died out, and the crucible and contents were taken out, Fig. 110 (page 1248). In this way extremely slow cooling was obtained, the effect of oxidation was minimised, and the size of the crystals and structure was in general increased, in some cases by ten diameters.

Cutting, grinding, and polishing.—The alloy was cut with a saw, and a smooth surface was obtained by drawing it downwards over the face of a smooth-cut file held vertically, the tang pointing

downwards.* The next stage of the operation consisted in rubbing the specimen on sheets of emery paper varying from 2 to 0000 in fineness. The papers from 0 to 0000 were moistened with paraffin oil. If the papers are attached to a quickly revolving wheel, a great amount of time and labour is saved. On each paper the rubbing was stopped immediately the marks of the previous paper had been obliterated. In some cases the rougher grades of emery paper could be omitted, and the surface ground down upon a flat Turkey-stone, using paraffin oil to moisten it. The specimen was next polished on broadcloth with rouge moistened with oil, using practically no pressure. In the alloys containing only a small percentage of copper, it was found that the best way to obtain a good polish and to remove the scratches due to the emery, and at the same time to prevent the spreading of the softer metal, was to use diamantine powder and oil, and to polish with the finger.

Etching.—The specimens were next placed in alcohol and thoroughly soaked, then washed and placed in a solution containing 1 per cent. nitric acid in water. In about 30 seconds the acid brings out the structure. The specimens were then taken out, washed, dipped in 1 per cent. hydrochloric acid to remove oxide of tin, again washed, soaked in alcohol, and dried. If the structure was not fully developed, the specimen was again etched. When the alloys contain a large percentage of copper, considerably stronger acid must be used for etching.

Isolation of Crystals in the 1 to 40 per cent. Cu alloys.—The alloy was placed in an ordinary gold-parting tube filled with 10 per cent. nitric acid, and allowed to stand till quite disintegrated. The acid was poured off and the residue washed. 10 per cent. hydrochloric acid was used to remove the oxide of tin remaining; but great difficulty was experienced in getting rid of the last traces. The crystals were then washed and dried. In most of those furnace-cooled alloys of which the eutectic formed a considerable

* Stead. Journal of the Society of Chemical Industry, March 1897, page 200.

part, a dark powder was obtained together with the crystals. Under the microscope the powder was seen to consist of minute bright plates with irregular borders. Their colour was the same as of the bright crystals, and it is probable that they formed one of the constituents of the eutectic.

Details and Description of Figures.—Plate 189 shows the recorder of the pyrometer, front and back view, which explain themselves. The whole in place and in working order is seen in Fig. 5.

Fig. 1 (page 1214) shows the freezing-point curves of the copper-tin series by Dr. A. Stansfield, published in the Fourth Report of Alloys Research Committee, 1897, Plate 10.

Fig. 2 (page 1216) is the composition curve of crystals isolated from alloys containing from 1 to 40 per cent. Cu; it is constructed by plotting the relation of the percentage of copper in the crystals to that in the whole alloy. The change in direction at 8 per cent. Cu is due to the introduction of the new constituent at that point. The curve can be only approximately right, owing to the great difficulty in isolating the crystals in a pure state.

Unless otherwise stated, the alloys have been slowly cooled on furnace top, and the magnification is 20 diameters, vertically illuminated ($\times 20$ diams. *v*). The letters *f. c.* denote furnace-cooled; *o* = oblique illumination; *v* = vertical illumination.

0 to 1 per cent. Cu.—On the addition of even 0.1 per cent. of copper to tin, a new constituent surrounding the grains of tin can be distinguished. As the percentage of copper increases, the amount of enveloping material increases also; and the tin grains decrease in size and number, until at about 1 per cent. Cu they entirely disappear.

When these alloys are cast, the grains of tin are greatly reduced in size. It appears also that the tin in crystallizing out retains some copper, or else that the eutectic contains more copper than when slowly cooled, because the proportion of grains of tin to eutectic in those alloys which have been cast seems greater than in those slowly cooled. Again, with 1 per cent. Cu the cast alloy shows no signs of the bright crystals, which are clearly seen when the alloy is cooled in the furnace.

Fig. 6, Plate 190, shows an alloy containing 0·25 per cent. of Cu, in which the grains of tin are seen enveloped in a dark constituent, the eutectic.

Fig. 7 is a 0·5 per cent. Cu alloy. The grains are much smaller than before, and are surrounded by a considerable amount of eutectic.

Fig. 8 is the same cast in an iron mould. The grains are very small, and the relative proportion of eutectic is greatly diminished.

Fig. 9. The copper has been increased to 0·75 per cent. The tin appears as dendrites and irregularly shaped grains. Most of the field is covered by the eutectic, in which the grains and dendrites of tin are seen to have crystallized. The dendrites have long axes with projecting grains, round, elliptical, and club-shaped.

Fig. 10 shows a curious structure often met with in 1 per cent. alloy.

Fig. 11 is the same deeply etched. The bright minute plates are probably those of the eutectic, which in places are abnormally large. It is possible that they may be the initial crystallization of the bright constituent which appears distinctly when the alloy is furnace-cooled.

Fig. 12 shows the 1 per cent. alloy *f. c.* The eutectic point has been passed: that is to say, there is more copper present than necessary to form the first eutectic of tin and copper. In the ground-mass occur small bright acicular crystals, whose section is rhombic. In many cases they are hollow, and are often terminated by long pyramids. They polish extremely well, are steel-coloured by ordinary light, but appear white by vertical illumination. They are hard but not very brittle, and easily polish in relief. Etching with dilute acid does not affect them, and on exposure they oxidise only slightly to a pale yellowish colour. Their width varies from 1-150th to 1-300th of an inch. They contain about 34 per cent. Cu. As they are but few in number, the eutectic in the 1 per cent. alloy must contain almost 1 per cent. of copper. A

vertical section of the alloy was weighed, dissolved in 10 per cent. nitric acid, the oxide of tin got rid of by weak hydrochloric acid, and the resultant crystals weighed; but not a trace of dark powder was obtained with them. Taking their composition as 34 per cent. Cu, 66 per cent. Sn, we can find the weight of copper contained in them, and hence the weight and percentage of copper in the eutectic. This proves to be 0.9 per cent.

Fig. 13 is the upper part of a 1 per cent. alloy *f. c.* near the outside.

Fig. 14, Plate 191, shows crystals isolated from a 1 per cent. alloy.

They are the largest obtained as yet.

When the 1 per cent. alloy is cast the mass appears to be homogeneous.

1 to 8 per cent. Cu.—As the copper is increased from 1 to 8 per cent. the bright hollow rhombic crystals become more and more numerous. At first they occur isolated; then they tend to form groups, which appear in section as three and six-rayed stars, composed of single lines of crystals. As the percentage of copper increases, these stars become more complex, each ray being composed of more than one line of crystals. The crystals become more ragged and less clearly defined, due for the most part to parallel growth.

Casting produces a network of very fine crystallites, which tend to set along definite directions, forming skeleton crystals. These become more and more interfering as the percentage of copper approaches 8 per cent., and the individual crystallites become larger. On separation by 10 per cent. nitric acid, a black powder is left behind after the oxide of tin has been removed. Under the microscope this appears to be composed of fine plates, which are evidently the crystallites.

Cooling in the furnace greatly increases the size of the bright crystals, and diminishes their number proportionately; but does not alter their other characters.

With 1.3 per cent. Cu, bright needle-shaped crystals are seen, and under the microscope the field appears very similar to Fig. 12.

Fig. 15, Plate 191, represents a 2.6 per cent. Cu alloy. The crystals have greatly increased in number, and tend to form groups, many of which in section show an axis with three arms equally inclined; in the 5 per cent. alloy, Fig. 16, the groups are clearly seen as characteristic six-rayed stars. The crystals in section are horse-shoe shaped, being generally hollow. Their rhombic shape is seen in Fig. 17, showing a 5 per cent. alloy furnace-cooled, in which the crystals happen to be cut across their long axis.

Figs. 18, 19 show several crystals isolated from a 5 per cent. alloy *f. c.*; they are similar to those from the 1 per cent. alloy *f. c.*, and like them tend to parallel growth.

Fig. 20 is a 5 per cent. alloy cast. The whole mass is composed of a fine network of minute crystallites. Six-rayed stars are seen, and each ray forms an axis of crystallization, from which bands of fine crystallites proceed till they meet and are continuous with those from the next ray or axis. The whole network or web is a true skeleton crystal, of which the crystallites all tend to set in definite directions. In other parts of the field figures of rhomboid form are seen, composed of bands of crystallites parallel to the boundaries.

Fig. 21 shows an 8 per cent. Cu alloy. The crystals spread across the whole field, and are more irregular in shape than in the 5 per cent. alloy. Six-rayed stars are frequent, but each ray is composed of more than one line of crystals.

Fig. 22, Plate 192, shows the same when cast. The crystallites are much larger and thicker than in the 5 per cent. alloy, Fig. 20. There is an evident tendency to crystallize along certain directions, as before; but as the crystals occur closely together, it is only in places that definite figures are seen.

9 to 40 per cent. Cu.—With 9 per cent. of copper a new constituent crystallizes out in forms similar in section to the crystals in the 1 to 8 per cent. alloys, but differing from them in never occurring hollow. On oxidation it becomes very dark, and is easily distinguished from the other two constituents of the alloy. In form it is plate-like, and good specimens show a tendency to

crystallize as basal crystals, probably rhombic ; around it crystallizes out the bright constituent characteristic of the 1 to 8 per cent. alloys, either as a rough envelope of fairly uniform thickness, or as projecting crystals. In the slowly-cooled alloys containing about 9 per cent. Cu, the difference between the constituents of the crystals can be seen only under high powers, when it is easily distinguished by its colour ; but when between 20 and 30 per cent. Cu is reached, oxidation shows a darker centre or core to the crystals. The probable reason why the new constituent cannot be easily made out in the lower alloys is because it does not readily oxidise. As the copper in the alloy increases, the copper in the new constituent increases, its freezing-point rises, and it becomes proportionately more oxidizable. The series is best studied when furnace-cooled, as the new constituent can then readily be seen forming the core of composite crystals.

As the copper approaches 40 per cent., the plate-like crystals are grouped together in parallel bunches, until at 40 per cent. Cu they are very thick and cover more than half the field. In the eutectic between them the small bright hollow crystals are seen.

Casting masks the composite character of the crystals, if in the lower percentage it does not destroy it ; for under 20 per cent. Cu the crystals cannot be resolved into two components under high powers. On dissolving out the eutectic by dilute nitric acid (1 in 10), a black powder is left behind in the alloys near 9 per cent. Cu, and in those near 40 per cent. a spongy brittle framework of crystals. The black powder consists of fine plates, which go to build up the skeleton crystals, as in the cast alloys containing from 1 to 8 per cent. of copper.

Fig. 23, Plate 192, shows a 10 per cent. Cu alloy. Under high powers the central core of many of the bright crystals is seen to be of a darker character, whilst from its side grow out crystals of the bright constituent.

Fig. 24 shows an isolated crystal from the 10 per cent. *f. c.* alloy. It shows the method of growing in parallel groups, forming in this way a large skeleton crystal.

- Fig. 25 shows a 10 per cent. Cu alloy, *f. c.* The characteristic horse-shoe or hollow crystals are abundant.
- Fig. 26 represents a rough section of the same alloy, which was exposed to the atmosphere for some time; the composite nature of these larger crystals is clearly seen.
- Fig. 27 shows the same alloy cast. There is a distinct tendency to form skeleton crystals, but no composite crystals could be discovered in the alloy. It is very similar to the 8 per cent. cast alloy, Fig. 22. If however the alloy be cast when pasty, amongst the network of fine crystals can be seen composite crystals. The 9 per cent. alloy behaves in a similar manner.
- Fig. 28 shows a 20 per cent. alloy. The crystals have increased in number and size; most are composite.
- Fig. 29 shows the same alloy, obliquely illuminated; the specimen is taken from the centre of the mass, where the crystals are larger. Several of the horse-shoe type are seen in the eutectic.
- Fig. 30, Plate 193, shows a 20 per cent. Cu alloy *f. c.* Composite crystals are seen on the right; while on the left are seen two crystals of the bright constituent, cut very obliquely across their long axes, thereby giving a drawn-out appearance to what would have been horse-shoe shaped, had they been cut more nearly to the normal to their long axes.
- Figs. 31 and 32 represent two crystals isolated from a 20 per cent. *f. c.* alloy, which show distinctly the difference in colour, texture, and mode of crystallization of the two components of each crystal.
- Fig. 33 shows a rough section of a 20 per cent. *f. c.* alloy, which has been exposed to the atmosphere along with Fig. 26. The crystals have been cut normal to their basal plane.
- Fig. 34 represents a 20 per cent. alloy cast, and shows a network of long lath-like crystals which are no longer composed of crystallites. Under high powers they are seen to be composite. There is a general tendency to crystallize in groups, which continues throughout this part of the series. .
- Fig. 35 shows a 30 per cent. Cu alloy. The composite crystals have grown much larger, and are beginning to interfere with one another.

Fig. 36. When cast the appearance is similar, but on a much smaller scale. This hair-like network produces a very tough alloy. The crystals are all composite.

Fig. 37 shows the surface of the cast 33 per cent. Cu alloy. In cooling, the eutectic has contracted and left the crystals standing above the surface of the ingot.

Fig. 38, Plate 194, contains 40 per cent. Cu. The plate-like composite crystals have become broad, due to multiple growth, and occupy most of the field. In the eutectic between them, the finer prismatic crystals are seen in section in the usual horse-shoe form.

Fig. 39. When cast, but little of the eutectic can be seen. The crystals are long, thin, and give the mass a highly fibrous appearance. The tendency to form groups is marked.

Fig. 40. The surface of the cast alloy shows several points from which crystallization has started, and the shrinking of the eutectic in solidifying gives a characteristic appearance.

41 to 61.7 per cent. Cu.—The difference between the alloy containing 40 per cent. and that containing 41 per cent. Cu is very marked. The crystals in the latter are small and lath-shaped, arranged more or less in groups, and separated from one another by eutectic. They are composite as before, but the white constituent surrounds the dark as an envelope of uniform thickness, not as a rough incrustation. No single prismatic crystals of the white constituent have been seen in the eutectic. The alloy is brittle, and apt to break in cutting; the brittleness increases with the percentage of copper. With each addition of copper the groups of crystals become more and more compact, and the amount of eutectic diminishes until at 56 per cent. Cu it disappears altogether.* The bright constituent of the crystals grows smaller and smaller; at 56 per cent. Cu it takes the place of the eutectic, and forms the ground-mass in which the constituent containing the higher percentage of copper has solidified. When 61.7 per cent. Cu is reached, the bright constituent disappears, and we have a

* Stead. Journal of the Society of Chemical Industry, June 1897, page 506.

homogeneous mass of Sn Cu_3 , probably a definite compound. It is crystalline, each crystal or grain having an orientation different from its neighbour's. It seems to have a cleavage.

Casting seems to harden and toughen these alloys, as it makes the groups of crystals more compact, and tends in the lower percentages to make the crystals themselves fibrous. The surface structure is often very beautiful, and is seen in places to be composed of long fibrous crystals, together with others of a curved and contorted nature. In the higher percentages of the group, casting produces the massive crystalline structure characteristic of cast lead, tin, and zinc, &c. Above 50 per cent. the eutectic cannot be distinguished, and the alloys become brittle, and hard to cut. It is almost impossible to illuminate numerous pittings of the prepared surfaces.

When the alloys are furnace-cooled, their appearance differs but little from that of the ordinary alloy. The structure appears to be simply magnified, although it seems that the re-arrangement of the constituent which first solidifies does not take place till the total copper exceeds 41 per cent.

Seeing that these alloys up to about 56 per cent. Cu show four breaks in their cooling curves, it would naturally be expected to find four different constituents in each. Three only however can be distinguished. Quenching below the first and second breaks gives a difference in structure only. As in the alloys containing 61·7 per cent. Cu and upwards, branch *e* of the complete freezing-point curve corresponds with a re-arrangement in the solid; and as the difference between the 40 and 41 per cent. Cu alloys is one of structure only, we may assume that the second retardation in the cooling curve of these alloys is one of re-arrangement also.

Fig. 41, Plate 194, shows the 41 per cent. alloy, and consists of bright lath-like crystals surrounded by the eutectic. There is a distinct tendency to form groups, which in

Fig. 42, the 43 per cent. alloy, is still more marked.

Fig. 43 shows the same alloy cast. The crystals have a highly fibrous appearance, and the groups are shorter and more compact.

Fig. 44 shows the cast surface of the 43 per cent. alloy; there is a characteristic fern-like structure quite distinct from that of Fig. 40.

Fig. 45 shows the 46 per cent. Cu alloy. The groups have become much more compact, and merge into one another.

Fig. 46, Plate 195, shows the 50 per cent. alloy, polished slightly in relief. There is a further merging of the crystals into one another. Each group of crystals has its own orientation.

Fig. 47 shows the same alloy quenched below the first break in Fig. 1 (page 1214). It has a distinct granular appearance.

Fig. 48 shows the same quenched below break 2. The crystals have formed groups, as in the slowly-cooled alloy, Fig. 46, each group having a distinct orientation.

Fig. 49 shows the 56 per cent. Cu alloy, in which etching has been carried far enough to distinguish the two constituents. The eutectic is missing.

Fig. 50 shows the 60 per cent. Cu alloy *f. c.* Oxidation shows the dark constituent surrounded by a matrix of the bright one.

Fig. 51 shows the alloy containing 61.5 per cent. Cu *f. c.* This alloy is extremely brittle, but cuts well with a file. Its structure is large, being composed of crystals with irregular boundaries. There seems to be a cleavage.

61.7 to 68.2 per cent. Cu, Sn Cu₃ to Sn Cu₄.—The changes which take place between these two points can be observed only when the alloys are very slowly cooled. Each addition of copper to Sn Cu₃ brings in more and more of the bright constituent Sn Cu₄. Branch *c* of the cooling curve determines the structures of the alloys to a great degree. Quenching and casting produce structures totally new. The alloys set as a whole at the first break, and tend to re-arrange themselves subsequently in the solid.

Fig. 52, Plate 195, contains 62.5 per cent. Cu *f. c.* Irregular patches and grains of the dark Sn Cu₃ are seen surrounded by the bright Sn Cu₄.

Fig. 53 is the 63 per cent. Cu alloy, and shows an increase in the bright constituent.

Fig. 54, Plate 196, shows the 64 per cent. Cu alloy. There is a large increase in the bright Sn Cu₄. The dark constituent in places has lengthened out, sometimes forming long irregular bands dividing one area from another.

Fig. 55 represents the 65 per cent. Cu alloy. More than half the field is covered by the bright constituent. Sinuous bands of the dark have increased, whilst its granular structure has gone. Under higher powers a new structure is noticed in places in the white Sn Cu₄.

Fig. 56 shows this structure. It closely resembles a eutectic, and accounts for the lowest break in the cooling curve, namely the horizontal branch of *e* running from 65 to 68 per cent. Cu in Fig. 1 (page 1214).

Fig. 57 shows the 66 per cent. Cu alloy *f. c.* There is a further increase of the bright constituent, the dark being still in the form of elongated masses and bands. The eutectic-like structure is still present in places, in the midst of the bright constituent.

Fig. 58 shows the same alloy slowly cooled. It would seem that the dark constituent has been endeavouring to arrange itself in definite directions. The eutectic is conspicuous.

Fig. 59 shows the 66 per cent. Cu alloy, quenched on break 1. There is a cell-like structure, with light coloured walls or boundaries. The background is composed of a network of a definite character.

Fig. 60 is the same quenched on solidification. The cell-like structure is marked, and the dark lines of the background are almost wanting. Hence it may be assumed that on solidification the structure is that of Fig. 60, but it immediately commences to change, if not quenched at that instant.

Fig. 61 is the same, quenched below break 1. The cell-like structure of Fig. 60 has gone, and this new structure has taken its place.

Fig. 62, Plate 197, is the same, quenched below break 2. It has all the characteristics of the slowly-cooled alloy, Fig. 58, Plate 196, excepting the eutectic. So that break 2 must mean the re-arrangement into the two constituents, and break 3 the eutectic.

Fig. 63 is the 66 per cent. Cu alloy cast on an iron plate. It is similar to Fig. 61, and shows that the re-arrangement into light and dark constituents has been forced.

Fig. 64 is the same alloy cast as an ingot. Large areas are seen of black and white. In each area the black lenticles are arranged in a definite direction. There is no sign of a eutectic.

Fig. 65 shows the 68.3 per cent. Cu alloy *f. c.* It is composed almost entirely of bright grains, more or less elongated. The alloy has been rather deeply etched to show the form of the grains. It has a conchoidal fracture, and is extremely brittle.

Fig. 66 is the same alloy cast on an iron plate. It consists of polygonal grains similar to those seen in a pure metal. Each grain has definite boundaries, more or less straight, with distinct orientation. Again, each grain seems to be made up of minute cubes, giving it a black and white appearance when deeply etched, like that of pure iron. This resemblance to a metal is further marked when viewed under a magnification of some 2,000 diameters, when each grain is seen to be built up of a network of grains arranged in a definite manner, generally as a skeleton with two axes at right angles. The skeleton-like appearance of the secondary grains is due to the etching material, which has eaten deeper into their edges compared with their centres.

Fig. 67 represents the ingot of the same alloy. The primary grains are larger than in Fig. 66, but are built up of secondary grains or cubes as before. The alloy thus has every appearance of a compound.

Fig. 68 is the same alloy quenched on solidification, that is, during break 1. Irregular rounded grains or patches of a dark material occur in a lighter matrix. Under a higher magnification, Fig. 69, the dark matrix is seen to pass gradually into the light material, which is composed of fine short needles. The whole represents a transition which becomes complete at the second break.

68.28 to 74.5 per cent. Cu.—Immediately the copper is increased above 68.2 per cent., the second eutectic makes its appearance, enveloping the polygonal grains of Sn Cu₄. As the copper increases, the grains split up into veins and dendrites, which attain their full development in the neighbourhood of 72 per cent. As the total copper increases, the eutectic increases also, the veins of Sn Cu₄ gradually disappear, and finally the dendrites go, leaving the mass entirely made up of eutectic about 75 per cent. Cu. The alloys are best studied when furnace-cooled. Above about 71 per cent. Cu their surfaces are seen to consist of a network of dendrites or skeleton crystals, resembling those seen on the surface of a pure metal. This network continues right up to the copper end of the series. It was soon noticed that the internal structure of the alloys from 70 to 75 per cent. Cu showed no trace of dendrites; and accordingly the surfaces of several were rubbed down and polished, so as to lay bare their internal structure. In each it was the same as that of the centre of the alloy, which shows that the dendrites have split up and re-arranged themselves after solidification, and all that remains of them is this surface structure.* Quenching proves that the second and third main breaks (branch *c*) of these alloys mean re-arrangement into dendrites and eutectic; but just below break 1 there occurs a small break which is difficult to explain. It leaves the outer curve at 68.3 per cent. Cu, and runs horizontally to about 74 per cent. It seems probable that it takes place in the solid also, because the appearance is identical of the alloys quenched on solidification, and of those quenched between solidification and break 1.

Casting masks the structure of the alloys in the lower percentages, and nothing but bright veins in a darker ground-mass can be seen under low powers. Under higher powers however the usual character can be seen. About 73 per cent. Cu, traces of the skeleton crystals seen on the surface of the furnace-cooled alloys can be observed in the centre of the ingot. They appear dark and structureless, as if they had not been able to resolve themselves into their two constituents.

Re-heating the furnace-cooled alloys to 700° C. (1,292° F.) and

* Heycock and Neville, Proceedings, Royal Society 1901, vol. lxxviii, page 171.

quenching them produces a structure similar to that of the cast alloys. Annealing after such a treatment restores the original structure.

Fig. 70, Plate 198, shows the 72 per cent. Cu alloy *f. c.* Large areas are seen with bright boundaries, and composed of bright dendrites and rounded grains set in a dark matrix, which is the eutectic.

Fig. 71 is the 73 per cent. Cu alloy *f. c.* The bright boundaries are getting smaller and the dendrites fewer.

Fig. 72 is the surface of the same, cut and polished. Etching has brought out the structure of the surface crystallization, and shows it to be complex.

Fig. 73 is the 73 per cent. slowly-cooled $\times 53$ diams. *v.*

Fig. 74 is the same alloy quenched on solidification; the dark grains of a rounded or irregular shape occur in a light matrix. Their relation to the first and to the minor break has not been settled as yet.

Fig. 75 is the same alloy quenched at 650° C., below these two breaks but above those of branch *e.* It shows a mottled appearance of light and dark, the whole being studded with minute white grains. The action commenced in the upper breaks is incomplete, and the white dendrites have been forced out as white grains.

Fig. 76 shows the same alloy quenched at 500° C. below the second main break. The structure is the same as in the furnace-cooled alloy. The ground-mass however, under ordinary powers, does not show a eutectic structure. Hence the second main break means the separation out of the veins and dendrites, and the last means that of the eutectic from the ground-mass.

Fig. 77 shows the 73 per cent. alloy cast as an ingot. It is a view of the upper part of the centre of a vertical section. The darker parts are the remains of the surface crystals of a slowly-cooled alloy. Under higher powers the structure of the remainder is the same as that of a slowly-cooled alloy.

Fig. 78, Plate 199, represents the furnace-cooled alloy, Fig. 71, which has been re-heated to about 700° C., quenched, and

annealed. The annealing has not been carried far enough, leaving the specimen in a transition state between a slowly-cooled alloy and one cast or quenched.

Fig. 79 shows the 74 per cent. Cu alloy *f. c.* The whole mass consists of eutectic, which crystallizes out in large grains or crystals with irregular boundaries, but with distinct orientation. The alloy is rather brittle, but cuts and polishes well. The bright veins have entirely disappeared, but here and there patches of the dendrites remain. These latter are few in number however, and show that the eutectic is almost reached.

Fig. 80 shows such a patch in the 74 per cent. alloy *f. c.* The general form of these dendrites is a three-rayed star. Many stars go to each patch, but in any one patch all the stars are set alike, and so a regular mesh is formed.

75 to 100 per cent. Cu.—When 76 per cent. Cu is present, two new constituents make their appearance, and the alloy assumes a yellow tint. It loses its brittleness. In section are found yellow grains, surrounded by a bright white border, set in the second eutectic, in which small bright white grains also occur. Now this eutectic of the 76 per cent. alloy is much larger in character than that of the 74 per cent. Cu specimen: which may account for the fact that the eutectic break rises some 30° C. as it passes from 74 to 75 per cent., Fig. 1.

As the total copper is increased, the yellow grains increase, forming dendrites and skeleton crystals; the white borders and grains merge together, and the eutectic decreases till at about 90 per cent. it disappears. The yellow grains become darker and darker, containing less and less tin in solid solution, till they reach copper colour. The light borders diminish and disappear, leaving only copper dendrites behind at about 95 per cent. These dendrites vary in composition from centre to outside, and so the centre etches a darker colour. They darken with increase of copper till 100 per cent. is reached, when we have the characteristic structure and colour of pure copper.

When the alloys are furnace-cooled, the structure is much enlarged, and the nature of the alloys becomes clear. Casting, on the other hand, masks the character of the alloys, and tends to make the copper grains solidify, containing a considerable quantity of tin. In this way the eutectic can be made to disappear considerably below 90 per cent.

Quenching shows that the upper break corresponds with the solidification of the copper, and break 2 with the solidification of the ground-mass, which splits up into a eutectic when branch *e* is reached. The meaning of the small and almost vertical branch of *e* running upwards from 75 to 77 per cent. Cu, Fig. 1, is not quite certain, but it most probably indicates the separation of the white grains from the ground-mass, as seen typically in the 76 per cent. Cu alloy *f. c.*

Fig. 81, Plate 199, shows a 75 per cent. Cu *f. c.* cast surface. Large dendritic crystals are seen with distinct forms. On cutting and polishing this surface, Fig. 82, no sign of these crystals was seen, but the alloy appeared granular, each grain being surrounded by a border of harder matter which polished in relief. The difference is probably that in the softer parts the eutectic has separated out, and in the harder it has been unable to do so.

Fig. 83 is the same *f. c.* alloy re-heated to a pasty condition and quenched. The large crystalline structure formed on the surfaces of these alloys has been set up, but the quenching has prevented it from re-arranging itself.

Fig. 84 shows the 76 per cent. Cu alloy *f. c.*, in which yellow and white grains make their appearance for the first time.

Fig. 85 is the same $\times 53$ diams. *v.* The three constituents, the large yellow grains of copper, the white grains and borders, and the eutectic, are easily distinguished.

Fig. 86, Plate 200, shows this alloy quenched at solidification. Small well-formed yellow dendrites occur in what appears to be a homogeneous matrix, which has been unable to arrange itself. It possesses however a minute cell-like structure.

Fig. 87 shows the 76 per cent. *f. c.* alloy re-heated to pasty and quenched. It resembles Fig. 83 in structure, but within the

centre of each arm of the crystals small rounded grains can be seen.

Fig. 88 is an example of the surface structure of one of these alloys, the 77 per cent. Cu *f. c.*

Fig. 89 is the same, cut through the crystals, polished and etched. It shows distinctly that the crystals have re-arranged their internal structure, and under a slightly higher power the eutectic is recognised. That the dendrites of copper have formed first is not evident in this alloy, but in the higher percentages it becomes clear.

Fig. 90 shows the 77 per cent. alloy cut through the centre. It is composed of polygonal grains, and each has a definite structure.

Fig. 91 is the 80 per cent. Cu alloy slowly cooled, whilst

Fig. 92 shows the same alloy, which has taken a considerably longer time to solidify. The dark copper dendrites and grains have considerably increased in number and size, and the amount of eutectic has decreased proportionately.

Fig. 93 is the same alloy quenched when liquid. Small irregular grains of copper are seen in a dark matrix which appears to be structureless.

Fig. 94, Plate 201, is the same alloy quenched below break 1. Large dendrites and skeleton crystals of copper are seen in a structureless matrix.

Fig. 95 is the same quenched below break 2. In places the matrix is structureless, but in general it has the coarse fibrous structure of a eutectic.

Fig. 96 is the centre of the same, etched with hydrochloric acid, causing the copper dendrites to appear whitish in colour. It shows the fibrous appearance of the eutectic, as if its formation had been forced.

Fig. 97 is the surface of the 80 per cent. Cu alloy cut, &c.

Fig. 98 is the same, and shows that with this percentage of copper, the dendrites of copper have directed the formation of the surface skeletons. It is possible that the alloy may have set as a whole at the upper break, and that the dendrites of

copper may have formed at break 2; but this hardly agrees with the fact that the period of break 1 increases in magnitude, whilst break 2 decreases.

Fig. 99 is the 80 per cent. Cu alloy cast, vertical section. It is very tough, cuts well, and polishes easily.

Fig. 100 is the same cast alloy annealed at about 750° C. It has here re-arranged itself markedly. The eutectic can now be seen and the copper dendrites have grown considerably. This seems to add weight to the view that break 2 corresponds with the separation of the copper. But this is not so. It proves however that the copper dendrites continue to grow *below* break 2, that is, in the solid.

Fig. 101 shows the 85 per cent. Cu alloy. The eutectic is becoming less, as the copper increases.

Fig. 102, Plate 202, is the same under a higher magnification. The specimen has been very slowly cooled.

Fig. 103 is the 90 per cent. Cu alloy.

Fig. 104 is the same cut through the surface.

Fig. 105 is the same very slowly cooled. No eutectic can be seen, only the copper skeletons with their white borders.

Fig. 106 shows a 95 per cent. Cu surface, and the characteristic structure of the alloys of about this percentage.

Fig. 107 is the 97·5 per cent. Cu alloy, and has the usual structure of copper that is not quite pure.

Fig. 108 represents the unalloyed top of a Cu alloy that has been chilled. It contains some 35 per cent. Sn, and 65 per cent. Cu. The structure is quite distinct from that of the ordinary 65 per cent. Cu alloy, Figs. 55 and 56, Plate 196.

Fig. 109 shows an alloy made by pouring molten tin into molten copper, and allowing them to diffuse in cooling. The whole range of alloys from 70 per cent. to over 80 per cent. Cu is here seen at once.

Fig. 110 (page 1248) shows the method of making the furnace-cooled alloys; it is a section through the two crucibles and their contents. The whole was placed in a fire, and when the alloy had melted, the fire was damped down with ashes, dampers were shut, and the whole allowed to cool slowly.

Figs. 111 to 118, Plate 203, show sections of the alloys 1 to 45 per cent. Cu. The difference of structure in Figs. 115 and 116 is due to the furnace-cooling of the latter. Fig. 117 has been very slowly cooled, and is intermediate between the two. The difference between Fig. 116 and Fig. 118 is also marked.

Since writing this Paper, the Report of the Committee, consisting of Mr. F. H. Neville, Mr. C. T. Heycock, and Mr. E. H. Griffiths, appointed by the British Association to investigate the nature of alloys, has been read at Glasgow. The work was directed towards

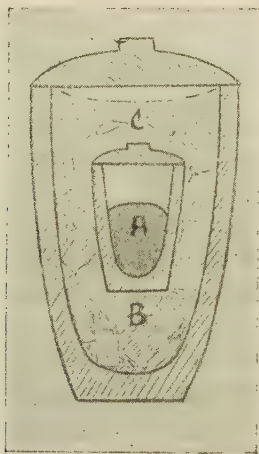


FIG. 110.

*Section through Crucibles and contents
for furnace-cooling.*

A. Alloy.

B. Charcoal.

C. Charcoal and
Charcoal Powder.

the verification of Roozeboom's theory of solid solutions in its application to the Copper-Tin Alloys, and embraced the series between 61 per cent. and 100 per cent. Cu or from Sn Cu_3 to pure copper.

Their work is of a most extensive and elaborate character. It confirms for the most part the cooling-curve published in the Fourth Report of the Alloys Research Committee, and proves conclusively that the alloys, between the two points mentioned, re-arrange themselves after solidification, and that the branch *d* represents a change in the solid state.

The Paper is illustrated by Plates Nos. 189 to 203 and 4 Figs. in the letterpress.

APPENDIX.

Illumination of Surfaces for Examination.—The only satisfactory method, except for very low-power work, is by the use of reflectors. For magnification with a 1-inch objective the Sorby-Beck Reflector is the best. In Fig. 119, Plate 203, this reflector is shown attached to the 1-inch objective, the whole standing upon the reflector case. It is composed of two parts, the one consisting of the parabolic reflector of Beck, the other of the small Sorby mirror set at an angle of 45° with the vertical. When it is desired to obtain oblique illumination, the Sorby mirror is turned out of play. Light falling horizontally upon the parabolic mirror is reflected at all angles, except the vertical, upon the surface of the metal or alloy to be examined. If this surface be perfectly flat, the whole of the light will be reflected at an angle, and none will enter the microscope tube. Hence a flat surface will appear black. This oblique illumination is used to advantage when etching has been deep, or where there has been polishing in relief.

For vertical illumination the small mirror is swung into place, covering about half of the lower objective lens. Then the horizontal rays of light from the lamp or other means of illumination fall upon the mirror at 45° , are reflected vertically downwards on to the polished surface of the metal or alloy, and thence up the microscope tube. All flat surfaces will then appear bright. Excellent vertical illumination can be obtained by a very simple method, described by Mr. J. E. Stead in his Paper on Practical Metallography.* He says, "a piece of blackened cardboard, fixed behind the object in a vertical position, and a cover-glass placed over the object at an angle of 45° , gives excellent illumination. The card and cover-glass can be temporarily attached to the object-glass slip by plastic wax. It only takes a minute to arrange."

* Proceedings, Cleveland Institution of Engineers, 26 Feb. 1900, page 97.

For high-power work, with objectives greater than 1 inch, the Beck illuminator is best. It is shown in Fig. 120, Plate 203, fitted to a $\frac{1}{4}$ -inch objective and standing on its case. It is screwed into the microscope tube, and thus lies between the eye-piece and the objective. It consists of a short tube with a thin slip of glass fastened in the axis of the small milled-head, by which the glass can be adjusted to 45° with the axis of the microscope. The light enters the side of the reflector by the circular aperture, is reflected downwards through the objective on to the specimen, and thence back again through the objective, reflector and eye-piece, thus giving vertical illumination. Where electricity is available an arc-light is best for high-power work, but a Welsbach gas-burner gives a very good illumination. For low-power work, a Welsbach is all that is necessary. A bull's-eye condenser should be used to concentrate the beam of light upon the reflector.

A multiple nose-piece attached to the microscope saves much time in changing objectives. Fig. 121, Plate 203, shows a view of a camera and stand, together with a microscope fitted with a nose-piece carrying a 1-inch objective with the Sorby-Beck reflector, and a $\frac{1}{4}$ -inch objective with a Beck reflector. This instrument is used in Professor Howe's Laboratory.

Discussion.

The PRESIDENT thought it desirable to point out exactly the relation in which the Paper, they had just heard, stood in regard to the work of the Alloys Research Committee. The series of experiments were carried out by the author under the direction of Sir William Roberts-Austen, and formed a complete series of examinations of tin and copper alloys, varying throughout from 1 per cent. tin with 99 per cent. copper to 99 per cent. tin with 1 per cent. copper. It was at first intended that the Paper should form one of the Appendices to the next Report of the Alloys Research Committee, but it was felt that it dealt with a complete investigation, not exactly connected with the main subject of that Report, and it was therefore thought better to bring it before the Institution as an independent Paper. The next Report of the Alloys Research Committee—which it was hoped would be brought before the Members early in the coming year—was a very important one, devoted chiefly to the effects of annealing steel, and it would afford ample scope for discussion in itself. Since Mr. Campbell's Paper had been prepared, the author had accepted an appointment at the Columbia University, New York, and he was therefore at present in the United States, but the Members had the advantage of the presence at the Meeting of Sir William Roberts-Austen, who would no doubt kindly reply to any points raised in the discussion.

Professor SIR WILLIAM C. ROBERTS-AUSTEN, K.C.B., Honorary Member, stated that Mr. Campbell's work on the microstructure of copper-tin alloys, especially as modified by quenching from a high temperature, was begun about two years ago in the laboratory of the Royal School of Mines. The results now published were submitted, in May last, to the Royal Commissioners of the 1851 Exhibition, from whom Mr. Campbell held a scholarship.

Turning to the original "cooling curves," which were published by the Alloys Research Committee of the Institution many years ago, Sir William claimed that the copper-tin curve was one of the earliest

(Sir William C. Roberts-Austen, K.C.B.)

series of curves in which the complex changes that occurred in *solid* alloys had been revealed. The nature of the successive and more complete curves of the copper-tin alloys, which had followed the older one, was then shown. They all pointed to the fact that profound molecular changes occurred in solid alloys when they were subjected to suitable thermal treatment, and from the engineer's point of view such changes were of the utmost importance, as they affected the industrial use of the alloys. This was exactly what Mr. Campbell has attempted to study. His work was not as complete, either at the copper end of the series or at the tin end, as he had hoped to make it, the reason for this being that he had been called away to conduct, under Professor Howe, experimental investigations at the Columbia University, New York. As regards the important alloys known as "gun-metal" and as "white" or "bearing metals," Dr. Rose would kindly offer some supplementary details. With reference to the work of other experimenters, Heycock and Neville had published some beautiful photographs of copper-tin alloys (containing about 79 per cent. of copper), both when slowly and when rapidly cooled. They had also, in a quite recent communication to the Royal Society (page 1264), studied the copper-tin alloys from the point of view of the phase rule of Gibb. This had already been done by the speaker and by Professor Bakhuis-Roozeboom for the carbon-iron series, as expressed in the complicated cooling curve of this series, which was one of the most interesting pieces of work the Alloys Research Committee of the Institution had published. He concluded by saying that as soon as the molecular changes in alloys were thoroughly understood, greatly extended uses would be found for alloys generally; hence the industrial importance of the work of the Committee, which would, so far as the Institution was concerned, be brought to an end by the publication of their forthcoming Sixth Report, which would be a very complicated one dealing mainly with the annealing of steel. The work would then be continued in the National Physical Laboratory.

Dr. T. K. ROSE said that although the Paper might at first sight appear to engineers to be somewhat too theoretical, nevertheless it

was one of those pieces of work that was necessary to be done, to prepare the way for the application to the industries of our knowledge of alloys. For example, taking the well-known gun-metal containing about 90 per cent. of copper and 10 per cent. of tin, an answer was required to the question—"What would happen when it cooled from a molten state to the ordinary temperature?" before it could be known what that metal was capable of. Solidification began in that alloy at about 1000° C. by the formation of crystals of nearly pure copper containing some tin, called by Messrs. Heycock and Neville the α crystals. As the temperature fell, those crystals continued to form, until at 790° C. (1454° F.) the mother liquor solidified, Fig. 1 (page 1214), forming what Messrs. Heycock and Neville called the β crystals. Below that temperature the alloy was entirely solid, but the α crystals went on growing at the expense of the β crystals, which continued to play the part of a mother liquor, although they were solid. Finally when the temperature had fallen to 500° C. (900° F.), the remainder of the β crystals split up into a "eutectic," consisting of a mixture of very small crystals of the α body and of what was probably Cu_4Sn . Now if at any of the intermediate temperatures, instead of being allowed to cool slowly, the mixture was quenched suddenly by being plunged into cold water, then the various bodies that existed at that particular temperature were, as it were, stereotyped and prevented from altering by the rapidity of the cooling. Widely different alloys were produced in this way, although they were all of the same composition. Mr. Campbell had determined the constituents of these alloys by microscopic examination, and it remained to determine their tenacity, their hardness, and their physical properties generally; for it was difficult to predict what would be the most useful alloys, until some such examination had taken place. In fact, the study of the effects of thermal treatment, already partly made in the case of steel, must be extended to other alloys.

The speaker then exhibited a number of slides, the first showing the 90 per cent. alloy which had been cast and then allowed to cool somewhat quickly. In this case the β body formed large meshes, but if the same alloy had been allowed to solidify slowly and had

(Dr. T. K. Rose.)

then been quenched, a totally different structure would have been obtained, consisting of small crystals of copper set in a dark matrix. This appeared to be of a very much higher tensile strength than the cast specimen. In both cases pure copper and pure tin were used in the preparation of the alloys. Other slides were shown of gun-metals containing 5 parts per thousand of oxygen and 1 per cent. of lead respectively, the thermal treatment of the specimens being identical with those mentioned above. All these specimens, however, tended to alter their structure very rapidly at ordinary temperatures, and care must be taken to remember this in examining the alloys. Outside the gun-metal series, interest in the copper-tin series centred chiefly in the anti-friction alloys, such as the "white metals" which contained from 80 to 90 per cent. of tin, 5 to 10 per cent. of copper, and usually 10 to 15 per cent. of antimony. The chief point about the metals, which were useful for bearing, was that they had hard grains set in a plastic matrix. In the case of the white metals the hard grains consisted generally of what used to be considered to be crystals of SnCu_3 , but which were more probably CuSn . The crystals were in the shape of long needles, sometimes forming star-like aggregates, some of which might be seen in the illustrations to the Paper, Figs. 16 and 21, Plate 191. These hard crystals had a very low coefficient of friction, and supported the load. They were embedded in a plastic mass which gradually yielded to pressure, and consequently could shape itself to an axle or a shaft. Figs. 122 and 123, Plate 204, which were due to M. Charpy, were illustrations of one of the alloys showing the star-like crystals and cubical crystals consisting of a compound of antimony and tin. The alloy was used for railway-car axles in France, and contained 83 per cent. of tin, 6 per cent. of copper, and 11 per cent. of antimony. Fig. 122 showed the structure produced by simply polishing it, and Fig. 123 showed that developed by etching with hydrochloric acid. Hard crystals of CuSn were seen in relief, the softer matrix having been worn away. By carefully examining Figs. 91 to 105, Plates 200-202, it would be seen that the value for anti-friction purposes of the alloys containing from 80 to 85 per cent. of copper and from 10 to 18 per cent. of tin, with from 0 to 2 per cent. zinc, could be explained in a similar manner.

Mr. F. H. NEVILLE said that Mr. Heycock and himself had been very much interested in the Paper, because it showed that two sets of workers had been going over the same ground quite independently and simultaneously. Messrs. Heycock and Neville had been saturated with the subject for nearly two years, and it was particularly interesting to hear it put in another man's words as in the Paper. The author started, like Mr. Heycock and himself, from the very beautiful curve of the copper-tin alloys worked out by Sir William Roberts-Austen and Dr. Stansfield; consequently, there must of necessity be a certain amount of similarity between their treatment of the subject and that of Mr. Campbell. He himself wished to say that he never realised how beautiful the Roberts-Austen and Stansfield curve was, and how much detail it contained, until they began to work with it, and then they saw how good it was.

Wherever their experimental methods were comparable with those of Mr. Campbell, they seemed to have obtained the same results. They recognised in the photographs the author had shown the same phenomena that they had observed themselves, the same bodies, the CuSn which Mr. Heycock and himself had isolated, although not quite in a pure state, and the Cu₃Sn which they had obtained absolutely pure from alloys of very different percentage composition. He thought there could be no doubt about the existence of those bodies, and, as Dr. Rose had explained, the CuSn fulfilled a very important function in the anti-friction alloys rich in tin. Their experimental methods had been very similar to the author's. They had taken a number of small ingots of alloy, quenched them at different temperatures, thus stereotyping the structure existing at each temperature, and obtained photographs very similar to his. It appeared to them to be very difficult to get a general grasp of the nature of the alloys, or at all events so to arrange the results as to make them intelligible to others, and in that respect possibly they had deviated from Mr. Campbell, and probably with some advantage. For, although in their experimental work their method had been so similar to the author's, they had in addition taken advantage of the theory of Professor Bakhuis-

(Mr. F. H. Neville.)

Roozeboom concerning the manner in which complexes solidified when they formed solid solutions, and by means of that theory they were able to state the results in a form which, though still difficult, was perhaps a little easier to grasp.

One of the principal new features in their diagram, Fig. 136 (page 1264), could be explained by Fig. 1 (page 1214) of the Paper. In that figure the upper curve *a d b* was the freezing-point curve, the curve giving the temperature at which each alloy *began* to deposit solid crystals. Any vertical line represented an alloy of a particular percentage composition, and if they followed such a vertical line from the top to the bottom of the diagram, they were really watching the alloy cool. Above the freezing-point curve the alloy was wholly liquid; when its temperature fell to the freezing-point curve, it began to solidify, and there *must be* a temperature at which it became wholly solid. If this latter temperature could be marked on the diagram for every alloy, another curve would be obtained, which would be the curve not of incipient solidification but of complete solidification. It would be a curve which might be called the melting-point curve, for by taking the cold alloy and heating it, it would begin to melt when it reached that curve. By a method which was not very accurate, but which was free from gross error, they had succeeded in tracing the melting-point curve, or curve of complete solidification, and he thought that it would be found a valuable addition to the figure. In their diagram, Fig. 136 (page 1264), the upper curve was the freezing-point curve, and below it was the curve of solidification or the melting-point curve. Whenever the alloy was above a certain temperature, between the freezing-point curve and the curve of solidification, it was a mixture of solid and liquid, and if quenched in that region of temperature would give large combs or skeleton crystals of a copper-rich material. It was no use quenching an absolutely liquid alloy, and in that they differed from the author; it was necessary, as Dr. Rose had said, to *stereotype a structure*, and it should be quenched when there was some solid. If quenched *between the curves* large copper-rich skeleton crystals would be found embedded in a tin-rich molten substance, which was liquid at the moment of quenching. It was a

curious feature of the solidification-curve that whenever it sloped, or was curved, the solidified alloy was a uniform mass of crystals which were themselves a solid solution. Hence all the bronzes with less than 10 per cent. of tin when quite solid were really uniform masses. He said they were uniform because they ought to be, but there was often a slender network of something else around the crystals due to imperfect transformation. From the point of view of persons who did not care for a half per cent., although mechanical engineers knew that a half per cent. was often a very important thing, these alloys were uniform, a uniform solid solution of tin and copper. On the other hand, whenever the solidification-curve was horizontal, as it was between 10 and 25 per cent. of tin, the solidified alloy was *essentially* a complex of two bodies, like a piece of conglomerate rock. He would not venture to attempt to explain the whole of the diagram, but wished to describe its purpose. All temperatures and compositions had been divided up into areas. By that means they were able to say that, if an alloy was in a particular area, it was made up of certain proximate constituents. The diagram really studied would enable anyone to read at a glance the condition that the alloy was in at any temperature. And, as both they and Mr. Campbell had shown, the changes in structure undergone by some of the alloys during cooling were very remarkable. Consider the alloy, a speculum metal, containing 30 per cent. of tin. Their diagram recorded the following facts about this alloy: that when it began to solidify at about 760° C. (1370° F.), the crystals which formed were solid solutions, richer in copper than the liquid; that it had wholly solidified at 700° C. (1260° F.), and that it was then a *uniform* solid solution. The diagram further showed that this uniformity in the solid alloy continued to exist until the temperature fell to 560° C. (1010° F.); but that at and below this temperature crystals of Cu_4Sn formed in the alloy, and that at ordinary temperatures the alloy was a conglomerate of Cu_4Sn and another material, which was much softer and richer in copper.

This example might suffice to indicate the aim of the diagram, which gave similar information concerning every alloy of the copper-tin series. [See page 1263.]

Mr. C. T. HEYCOCK confirmed what had been said by Mr. Neville, and thought it was specially interesting that two people, who had been working by different methods and in different ways, should arrive at the same result.

Mr. J. T. MILTON said that for some time past he had taken a great interest in the question of the microscopic structure of metals, and amongst other metals he had worked upon the copper-tin alloys. Of these he had confined his attention to the alloys which came under the notice of the practical engineer, namely, the so-called "gun metals" and the "white metals." He thought the members were exceedingly indebted to the Alloys Research Committee for the work they had done, especially with regard to the cooling curves. Those shown on the wall diagram* were to his mind most wonderful curves. Each of the lines showed certain physical conditions of a definite alloy, and enabled one to see what changes took place in the molecular structure of the metal. The breaks in the curves showed what might be called the latent heat of fluidification. Sir William Roberts-Austen, in one of the earlier Reports, had shown that in the cooling curve of pure gold the break was absolutely horizontal, and had pointed out that when the break departed from the horizontal line it was because the metal was impure. Whenever the break of one of the cooling curves was other than horizontal, he (the speaker) thought it would be found that the metal did not crystallise out with a uniform composition. It really confirmed what the author had said with regard to the first solidification which took place in gun-metals, namely, that the dendritic forms were not uniform throughout their structure, but contained more copper in their central portions. He thought the same thing happened with regard to the white crystals in the 8 per cent. and poorer alloys. Another important point to engineers, brought out by the Paper and by some of the earlier Reports, was the great difference in the mechanical properties of metals, resulting from different thermal treatments. The author had shown that, in

* *Third Report*, 1895; Fig. 10, Plate 41.

what he called "cast" metal, but which the speaker would prefer to term "cast on chill," the grain was exceedingly small; but when the metal was slowly cooled, it was usually much larger. That happened with every alloy. If metals were cooled very slowly from their fluid condition, some parts of them crystallised out earlier than others, and segregated together into large grains. The effect of gravity then came in, and in some instances separated the different portions; and instead of getting a uniform casting, a casting was obtained in which the upper part contained the lighter portions and the lower part the heavier portions. That was very common with the white metals, and occurred to a marked extent in some of those which were best known. The speed of cooling alloys was another point which was important in connection with gun-metals. When the first solidification took place and the first or yellow grains separated out, the mass was like a solid sponge or network, with the more fluid portions interspersed throughout. Referring to the diagram, Fig. 1 (page 1214), it would be seen that at 1000°C. , or a little below it, only the yellow grains were solid, and that during the time the metal was cooling down to about 800°C. (1450°F.), no further solidification took place. During this fall of temperature however, the metal was shrinking, and not only each individual grain but also the volume of the still liquid portion became smaller. The liquid part therefore had a tendency to settle down into the bottom of the mould, and the upper portion of the casting would remain spongy. From that point of view he thought the best and soundest castings were to be obtained, when the conditions of casting were such as to cause the temperature to fall as quickly as possible. He had never seen a piece of ordinary gun-metal casting that appeared to be sound under the microscope. Besides the vacuities caused by the shrinkage, he had always found spots which he had put down to oxide. He thought that they were due in some measure to the fact that copper when fluid, as was well known to all metallurgists, dissolved oxide of copper and maintained it in a fluid form. It was with a view of getting rid of this oxide of copper that the process of "poling" was introduced. He felt sure that the copper of the gun-metal in melting took up oxide, and while the copper and tin were fluid, the oxide also was fluid and

(Mr. J. T. Milton.)

dissolved in them; when however the copper solidified out, some of the oxide of copper became extruded. He always found the little spots of oxide were practically coincident with the positions of the matrix or eutectic, or the more fluid portion of the gun-metal between the yellow grains, and did not occur in these grains themselves. With regard to the preparation of specimens of the softer metals, in cutting up soft metals containing hard portions it was necessary to be exceedingly cautious and very patient, otherwise the hard portions were dragged through the softer matrix, and a wrong sort of image obtained. After sawing the metals, it was well to first rough-file the specimens to remove any portion dragged by the saw, and then to smooth-file them, always keeping the files wet with water. Carborundum powder was very sharp and cut without much dragging, as did also diamantine.

Mr. Milton then exhibited some slides to illustrate the remarks he had made. These are represented in Plate 205. The magnification in all cases is 40 diameters. Fig. 128 shows the separation which takes place by the action of gravity in one of the well-known white metals, when slowly cooled. The small granular portion is of greater density than the parts which appear light in colour, and settles to the bottom.

Fig. 129 shows the influence of the rate of cooling upon the structure of an alloy containing 8·5 per cent. copper and 91·5 per cent. tin. The left-hand portion shows the structure when the metal is cast on chill, the right-hand when it is slowly cooled.

Figs. 130 to 134 show the structure of alloys of copper and tin containing 4, 2, 1, 0·5 and 0·25 per cent. copper respectively. In all these sections the SnCu can be distinctly seen, but in diminishing proportions.

Fig. 135 is a section of the tin used, rather more deeply etched than the other specimens. It shows the granular structure of the tin. In Fig. 134 the etching was also sufficiently prolonged to indicate the similar granular structure of the matrix.

It was with some diffidence that he ventured to differ from the author as to the structure of the alloys at the tin end of the series. From the experiments which he had made, he had come to the

conclusion that the lower eutectic did not exist, and that the matrix of the lower alloys was either pure tin or more probably tin with a very small amount, less than 0·25 per cent., of copper in solid solution. In making a series of alloys with 4, 2, 1, 0·5 and 0·25 per cent. copper respectively, he had been able to observe distinctly free spots of SnCu in all of them, although of course in the lower grade alloys the proportion of this compound was small. The tin he had used in making these alloys had been kindly furnished for the purpose by Mr. J. Dewrance, and was the purest tin commercially obtainable, and was certainly free from copper. It would be noticed from the slides that the tin itself showed a granular appearance similar to the 0·5 and 0·25 per cent. alloys of the author, while the 0·25 per cent. alloy not only showed the presence of the SnCu he had referred to, but also showed a somewhat granular appearance of the matrix of tin. In this case the granular appearance was due to the etching being carried rather farther than was necessary to show up the CuSn portion of the structure.

The PRESIDENT expressed the indebtedness of the Institution to Mr. Merrett, who, in the absence of Mr. Campbell, had aided very materially in preparing the Paper for presentation. Without Mr. Merrett's assistance, there would have been very great difficulty in getting it ready for that meeting. The discussion, together with written communications, would be submitted to the author who would reply to them in due course.

Communications.

Mr. BERTRAM BLOUNT, in sending four photo-micrographs of copper, wrote that these photographs, which had been prepared by Messrs. Stanger and Blount's chief assistant, Mr. S. Dickson, might serve to supplement the series given in the Paper, as they represented copper of ordinary commercial purity and also the metal almost chemically pure. The following is a description of them:—

(Mr. Bertram Blount.)

Fig. 124, Plate 204. The pure copper, according to the result of a most rigorous analysis, contains 99·961 per cent. of Cu, and was prepared electrolytically by the Elmore process. Its enlargement is 115 diameters, and at this amplification it has a fine close structure not definitely crystalline. It will be understood from its mode of preparation that this metal is in the condition in which it was deposited, and has not been fused.

Fig. 125. A second specimen is shown of the same metal fused and cooled in hydrogen. In this case the structure consists of crystals of pure copper so large, that even with the moderate amplification of 40 diameters a single crystal occupies almost the whole field. The junctions of the crystals are quite sharp, proving that no fusible alloy or eutectic is present, as indeed would be predicted from the purity of the metal.

Fig. 126. A contrast is afforded by the next specimen, which is of good fire-box copper containing 99·54 per cent. of Cu. This was cut direct from a fire-box plate in the condition in which it would be used. The structure is definitely crystalline, but it will be seen that there are numerous aggregations of matter other than copper, forming dots and bands. These doubtless represent fusible alloys of the impurities with some part of the copper itself. On account of the metal having being worked in the manufacture of the plate from the ingot, the structure is more deformed and confused than would be the case with a cast metal.

Fig. 127. A piece from the same sample was fused in hydrogen, and allowed to cool slowly. The photograph of this specimen is enlarged to 40 diameters, and displays the separation of the alloying material from the relatively pure copper much more conspicuously than does the worked metal. The systematic study of such commercial metals and the correlation of their structure, with the observations of their behaviour in practice, cannot fail to yield results of importance to the mechanical engineer.

APPENDIX TO MESSRS. HEYCOCK AND NEVILLE'S REMARKS (page 1255).

Messrs. Heycock and Neville, in sending a description of their diagram of the copper-tin alloys, wrote that the curve diagram, Fig. 136 (page 1264), and photo-micrographs, Figs. 137-139, Plate 206, were reproduced by permission of the Royal Society.*

The diagram, Fig. 136, aims at stating the nature of every alloy of the copper-tin series, not only at ordinary temperatures, but at all temperatures. Temperature is measured vertically, and is expressed in degrees Centigrade by the vertical scales at each end of the diagram. The percentage of tin in the alloy is measured from left to right, and is given by the two scales at the top of the diagram. The upper scale of unequal divisions gives the percentage by *weight of tin*, the lower scale, of equal divisions, corresponding to the vertical lines ruled on the diagram gives the *atomic percentage* of tin in the alloy. This scale practically gives the chemical formula of the alloy; thus the number 20 indicates that the alloy contains 20 atomic weights of tin out of every 100 atomic weights present, so that its formula is $\text{Cu}_{80}\text{Sn}_{20}$, or more simply, Cu_4Sn .

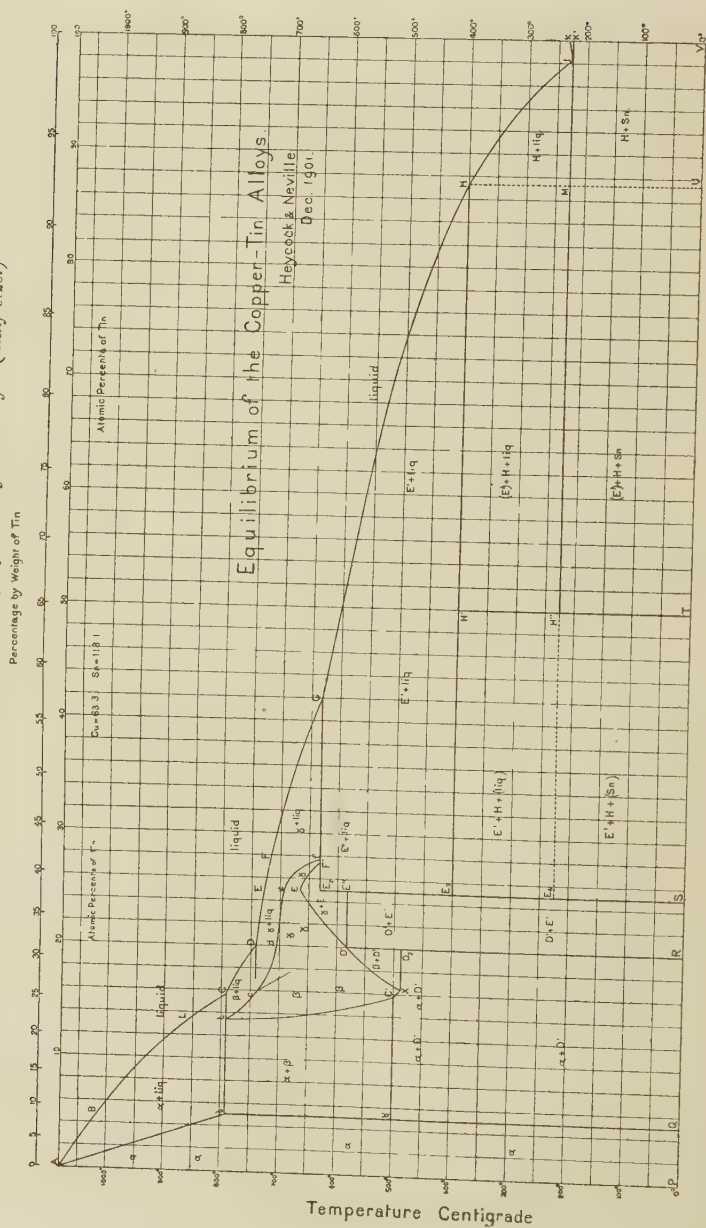
It is evident that a point on the diagram stands for a definite alloy at a definite temperature, while a vertical line defines the composition of an alloy, but does not state its temperature.

The curve ABLCDEFGHIK is the freezing-point curve, called by Professor Bakhuis-Roozeboom "the liquidus," because when the temperature of an alloy lies above this line, the alloy is wholly liquid.

The line AbcdefE₂E₃H'H'IK' is the "solidus," so called, because when the temperature of an alloy lies below the solidus, the alloy should be wholly solid. The "solidus" might be called the "melting-point curve," for if a cold alloy is gradually warmed, it will begin to melt when its temperature is that of a point on the solidus. Whenever an alloy is in the region of temperature between the solidus and the liquidus, it is partly solid and partly liquid, consisting of skeleton crystals immersed in a mother liquid which is richer in tin than the crystals. These skeleton crystals can be detected by chilling an alloy, when its temperature lies between the

* Proceedings of the Royal Society 1901, vol. 69, page 322.

(Messrs. Heycock and Neville.)

Fig. 136.—Reproduced from *Proceedings of the Royal Society. (Half size.)*

"solidus" and the "liquidus," but they do not always exist in slowly cooled alloys.

The remaining curve of the diagram, the curve $lC'XD'E'F'$, is Austen and Stansfield's curve of changes that take place in the solid alloys. These three curves, together with horizontal and vertical lines drawn through the intersections and singular points of the curves, enable one to divide the whole area into smaller compartments. Each of these compartments corresponds with a particular structure in the alloys, and so long as the point representing the alloy lies in a particular compartment the alloy possesses the structure peculiar to that compartment. Consider the bronze containing 7.5 per cent. of tin. While its indicating point lies in the compartment AbC , that is between the temperature $1,025^{\circ}$ and 850° C. ($1,880^{\circ}$ and $1,560^{\circ}$ F.), it will be a mixture of alpha crystals and a liquid richer in tin; while as soon as it comes into the compartment $APQb$, it should consist of a uniform mass of alpha crystals. No doubt the alloy if cast and cooled more or less rapidly would not be quite uniform (on account of imperfect transformations during cooling), but although Messrs. Heycock and Neville have not tried it, they believe that the cast alloy could be made uniform by rolling and annealing. On the other hand, the alloy with 20 per cent. of tin could never be made uniform, for when in the compartment $bb'C'l$ it is a complex of crystals of two substances differing a good deal from each other, and when it falls to the compartment $b'QR$, although it has undergone further change, it is still a complex. No amount of annealing or rolling will make it other than a complex.

The alloy containing 30 per cent. of tin is one of a group that undergoes very remarkable changes of solidification. Three figures, Plate 206, are given which are reproduced from Messrs. Heycock and Neville's Paper in the Proceedings of the Royal Society (Vol. 68, Plate 3), which illustrate the changes.

Fig. 137 is of the internal structure in a sample chilled midway between the solidus and the liquidus. The large copper-rich skeleton crystals, dark in the photograph, are seen embedded in a tin-rich mother substance which was liquid at the moment of chilling. Fig. 138 is that of a sample of the alloy chilled below

(Messrs. Heycock and Neville.)

the solidus, but above the line D'E'. The alloy is now very uniform, consisting of grains of a solid solution; the grains are chemically all alike, but as they differ in orientation, it is possible by etching to distinguish them from one another. This state of chemical uniformity continues as the alloy cools, until the line D'E' is passed, when the substance D', or as they think, Cu_4Sn , crystallises out of the solid solution. Fig. 139 shows the white tin-rich bands and rosettes of this body. The same body can be seen in Mr. Campbell's Fig. 76, Plate 198. The three alloys, of which photographs are given, were not etched, but the pattern was developed by heat-oxidation. Instead of examining the changes which other alloys undergo as they cool, the various substances, or *phases* which exist in the chilled or the slowly cooled alloys, will be briefly considered.

The substance alpha is not a definite chemical compound, but is a solid solution of tin and copper, which varies in composition from pure copper to copper with rather less than 10 per cent. of tin; but all the alpha crystals are alike in form. There are very good examples of skeleton crystals of alpha in Figs. 92 and 94 of Mr. Campbell's Paper. In Fig. 92 the alpha skeletons are dark, and in Fig. 94 they are light, but this is due to differences in the orientation of the grains; and the fact that in Fig. 92 the lines of crystal make angles of 60° with each other, while in Fig. 94 they make angles of 90° , is due to the same cause.

The substances β and γ .—These, also, are solid solutions of copper and tin, which appear to differ from each other in crystalline form. There are no β crystals containing less than about 22 per cent. by weight of tin, and the γ crystal richest in tin contains about 42 per cent. of that metal. Mr. Campbell's Paper does not contain a good example of these crystals, but the dark skeletons in Messrs. Heycock and Neville's first figure of the quenched alloy containing 30 per cent. of tin are β or γ crystals. Neither β nor γ is ever found in a slowly cooled alloy.

The substance D'.—They believe, and so does Mr. Campbell, that this body is the chemical compound Cu_4Sn . It is remarkable for

the peculiarity that it never crystallises from the liquid, but only begins to form when the solid alloys have cooled considerably below their temperature of complete solidification. The white rosettes and bands of their third figure of the 30 per cent. alloy consist of this body, and it can be seen, though not very well, in Mr. Campbell's Fig. 76, Plate 198.

The body E'.—This crystallises in plates, which seen edgewise often look like bars. The white bars in Mr. Campbell's Figs. 35, 38 and 40 consist of E'. They have isolated the plates of E' from a number of different alloys, and in several cases found them to be the pure compound Cu_3Sn , but it is possible that sometimes the plates of E' contain more tin dissolved in solid solution in the Cu_3Sn .

The substance H.—This occurs as a margin bordering the crystals of E' in all slowly cooled alloys between 39 and 93 per cent. of tin. The effect is clearly seen in Mr. Campbell's Fig. 26, Plate 192. In the alloys containing less than 7 per cent. and more than 2 per cent. of copper, the H crystals occur without a core of E', but their occasional hollow shape suggests that, when the alloy began to solidify, small nuclei of E' formed which were redissolved. Mr. Campbell's Figs. 17, 21 and 25 show this H very well. H is the hard body in the copper-tin alloys which are used as anti-friction metals. Their own analyses, those of Mr. Campbell and of previous workers, all point to the conclusion that pure H is the compound CuSn , but they are not aware that anyone has separated crystals which on analysis proved to be quite pure CuSn .

It will be noticed that in some of the compartments the presence of three substances is indicated, but that the symbol of one of the three is placed in brackets. This is done to show that the bracketed substance is an intruder, whose presence is due to the imperfect completion of reactions taking place in a solid.

It might be thought that only the lower compartments of the diagram, which deal with the condition of the alloy at ordinary temperatures, could be of use to mechanical engineers; but Messrs. Heycock and Neville venture to differ from this view, as they believe

(Messrs. Heycock and Neville.)

that the upper part of the figure will be found to throw light on the probable consequences of such operations as rolling, chilling, and annealing.

The above is by no means a complete account of the information conveyed by the diagram, but it is hoped that it may suffice to make it intelligible and useful in connection with Mr. Campbell's Paper.

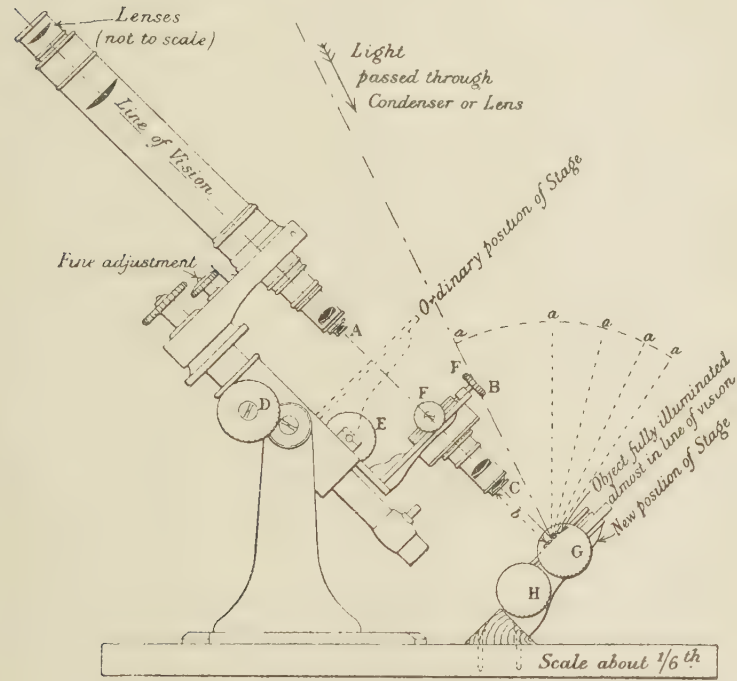
The authors wish to add that although they have complete confidence in the general accuracy of the diagram, yet it must be borne in mind that the shape of the solidus has as yet only been determined by approximate methods, and that further work will possibly somewhat alter the shape (but not the general character) of this curve, as well as the position of the point *b*.

Mr. DAVID JOY sent a sketch, Fig. 140, showing an arrangement of a microscope which he found it necessary to make some years ago, when examining steel forging fractures at Barrow-in-Furness. It was for use with opaque objects—such as in slicings of granite to get the carbonic acid globules visible—that he wanted room under the objective to get in a flood of direct condensed light. Of course in using the usual high power of objectives like a $\frac{1}{4}$ -inch, there was no room at all to get light between the object and the object glass, so he employed a low-power 3-inch objective next to the object, and this gave plenty of room to get an almost vertical ray of light. This objective was carried on the sub-stage usually employed for illuminators, having both centralizing screws and focus adjustments. Then he again magnified the image so obtained by a $\frac{1}{3}$ -inch objective mounted in the usual place, so getting a sort of double compound arrangement, which answered perfectly. He mounted the usual object stage (taken from above) on a block of wood below, thus having the adjusting movements in both directions.

Mr. CAMPBELL, in reply, wrote that when the work was started, an explanation of several of the branches of the freezing-point or cooling curve, Fig. 1 (page 1214), had not, to his knowledge, been satisfactorily given; and it was in striving to find this explanation that the author had been employed during the past two years. He was extremely

FIG. 140.

Arrangement for examining opaque objects (Joy).



A.— $\frac{1}{2}$ -inch objective, being second magnifier, magnifying the image made by the first objective C.

B.—Sub-stage usually used to carry illuminators, now used to carry first objective of low power, allowing room for full illumination, say 3-inch focus.

C.—3-inch objective magnifying the fully illuminated object.

D.—Milled handle to focus tube with $\frac{1}{2}$ -inch objective.

E.—Milled handle to focus sub-stage with 3-inch objective.

F F.—Milled handle to centre stage.

G.—Milled handle to adjust object stage laterally.

H.—Milled handle to adjust object stage to and fro.

a a a a.—Scope of external illumination.

b.—Clear space to get in light.

(Mr. Campbell.)

pleased to find that the main results had proved comparable with those of Messrs. Heycock and Neville, for whose work he had the greatest admiration. Their diagram, Fig. 136 (page 1264), which unfortunately he had not had an opportunity of seeing before his work had been submitted to the Institution, explained nearly all the points of difficulty he had met with.

Dr. Rose (page 1253) had very clearly explained what happened when the 90 per cent. copper and 10 per cent. tin alloy cooled down from the liquid state. The author was unaware of the fact that below 790° C. ($1,450^{\circ}$ F.) the crystals of copper (α crystals) went on growing at the expense of the ground-mass (β crystals) to any great extent. This view of the case explained Figs. 99 and 100, Plate 201. In Fig. 99 the 80 per cent. copper and 20 per cent. tin alloy was seen as it appeared when cast in a small cold iron ingot mould; the long fine dendrites of copper (α crystals) appeared in a lighter ground-mass, presumably β rich in α . On account of the rapid cooling, only a part of the copper had been able to separate out. The ground-mass had not been able to re-arrange itself. In Fig. 100 was seen the same alloy annealed at about 750° C. ($1,350^{\circ}$ F.). The crystals of copper (α) have grown considerably, at the expense of the ground-mass, which under a higher magnification was easily seen to be composed of the eutectic, this re-arrangement of the ground-mass into a eutectic taking place at 500° C. (900° F.).

With regard to the "white metals," so well worked out by Charpy, it was interesting to note that nearly all of them used for anti-friction purposes contained less copper than that required to form the complex crystals found in the alloys containing between 8 and 41 per cent. Cu of the copper-tin series, Figs. 31, 32, and 33, Plate 193. In other words, the crystals of the copper-tin compound generally had a composition between 34 and 44 per cent. Cu, Fig. 2 (page 1216).

In respect to what Mr. Milton said (page 1258) about the cooling of gun-metals—namely, that during the time the metal was cooling down from about $1,000^{\circ}$ C. to about 800° C. ($1,800^{\circ}$ F. to $1,440^{\circ}$ F.) no further solidification took place; the author was of opinion that this was not the case. He felt sure that Dr. Rose's explanation was

the right one, that the crystals continued to form until the mother liquor solidified at 790° C. ($1,454^{\circ}$ F.). Referring to the lower eutectic, whose existence Mr. Milton doubted, most of the workers upon the alloys of copper and tin mentioned it definitely. Charpy, in his Paper on the "Microscopic Study of Metallic Alloys,"* followed Le Chatelier's cooling curve, and placed the first eutectic at 3 per cent. Cu. He described it as very delicately laminated, and said: "Alloys containing from 0 to 3 per cent. Cu are very soft.... long dendrites may be detected, however, probably of tin, surrounded by a matrix, in which some very thin, hard crystalline trails (trainées) are discernible." These crystalline trails of Charpy's are the hard CuSn constituent of the eutectic. The author had recently repeated the work on the tin end of the series, and at 0.9 per cent. Cu in a furnace-cooled alloy found the whole mass to be laminar, exactly resembling the first eutectic alloy of the Sb-Cu series. Below 0.9 per cent. Cu, tin crystallised out as dendrites in a matrix composed of the alternate soft tin and hard plates or needles of SnCu. At 0.1 per cent. Cu this matrix was quite distinct, and when this alloy had been diluted with an equal weight of pure tin, it could still be discerned when very carefully treated. Mr. Bertram Blount's description (page 1262) of the appearance of pure copper in the condition of deposition was extremely interesting, since the author had recently examined some electro-copper 99.9 per cent. pure, prepared by the Nicholls Chemical Co. of Long Island. With ordinary etching, no structure of a crystalline character could be seen, but by using strong nitric acid, a coarsely crystalline structure was brought out in a most marked way. Figs. 141 and 142, Plate 206, showed this pure copper just as it came from the depositing tank; a section was cut and polished in the usual way. It was then dipped in strong nitric acid and quickly washed. The process of etching was repeated till the true crystalline structure of the metal, consisting of large polygonal crystals distinctly oriented, was clearly seen. Fig. 124, Plate 204, showed what were commonly known as mixed crystals; that is to say, cooling had not been prolonged sufficiently

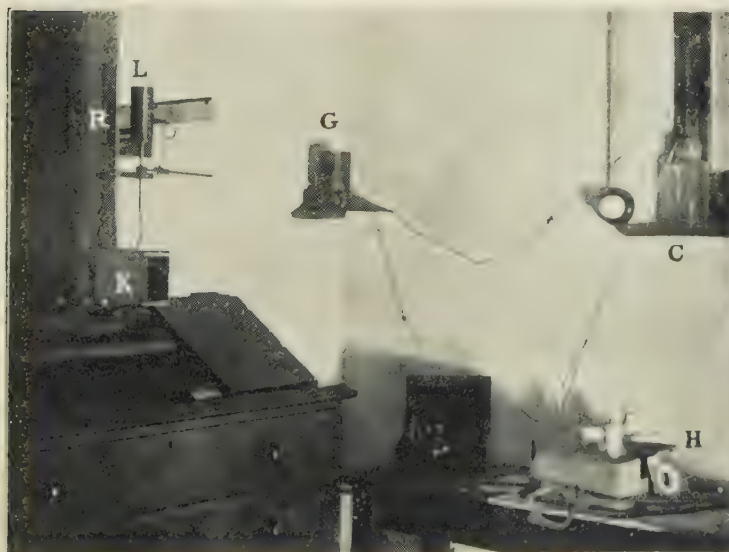
* "Metallographist," vol. i, page 194.

(Mr. Campbell.)

to allow diffusion to establish a complete equilibrium. Given sufficient time in cooling, the crystals in Fig. 124 would appear as uniform as those in Fig. 122.

In illustrating this Paper the original photographs had to be reduced, generally from 33 to 20 diameters, and consequently several were indistinct. This was specially the case in those alloys containing between 68 and 74 per cent. Cu.

In conclusion, he wished to express his gratitude to Sir William Roberts-Austen and to Mr. Merrett for their great kindness, not alone in seeing the Paper through the press, but also for many valuable suggestions offered during the progress of the work at South Kensington.

*Pyrometer-Recorder.*Fig. 3. *Front.*Fig. 4. *Back.*Fig. 5. *In place and in working order.*

L. Light.
R. Recorder.
K. Clock.

G. Galvanometer.

C. Cold Junction
of Thermo-Couple.
H. Hot Junction
of Thermo-Couple.

Fig. 6.

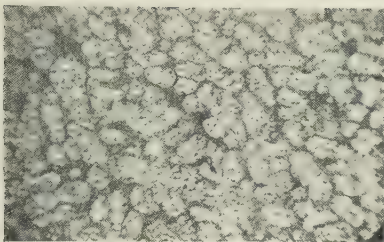
0.25% Cu. $\times 20$ diams. v.

Fig. 7.

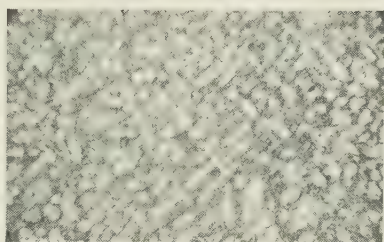
0.5% Cu. $\times 20$ diams. v.

Fig. 8.

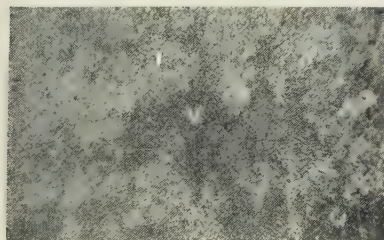
0.5% Cu. Cast. $\times 20$ diams. v.

Fig. 9.

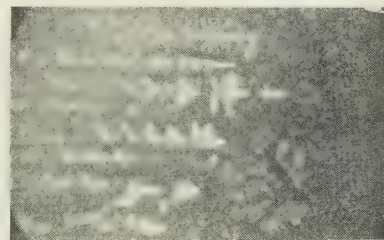
0.75% Cu. $\times 20$ diams. v.

Fig. 10.

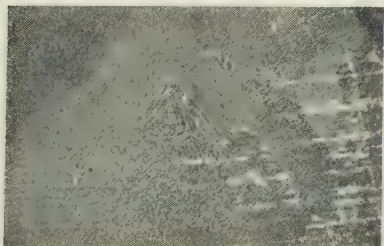
1% Cu. $\times 20$ diams. v.

Fig. 11.

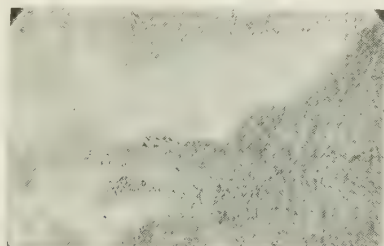
1% Cu. Deeply etched, $\times 20$ diams. o.

Fig. 12.

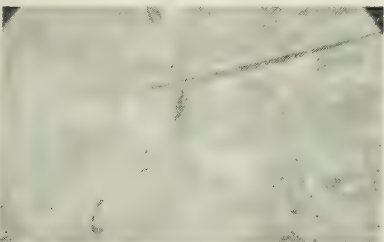
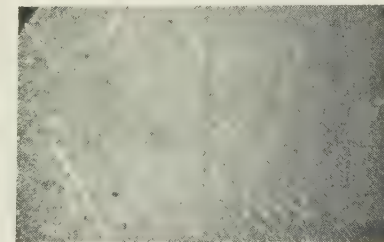
1% Cu, f.c. $\times 20$ diams. o.

Fig. 13.

1% Cu, f.c. Upper side. $\times 20$ diams. v.

f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

Fig. 14. Crystals.
1% Cu, f.c. × 20 diams. o.

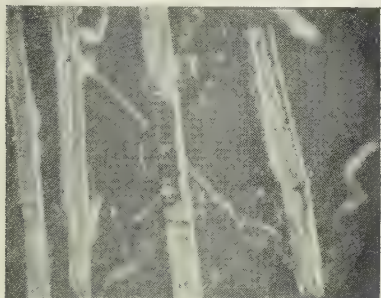


Fig. 15.
2.6% Cu. × 20 diams. v.

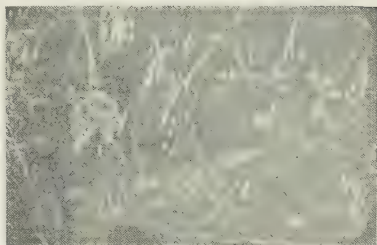


Fig. 16.
5% Cu. × 20 diams. v.



Fig. 17.
5% Cu, f.c. × 20 diams. v.

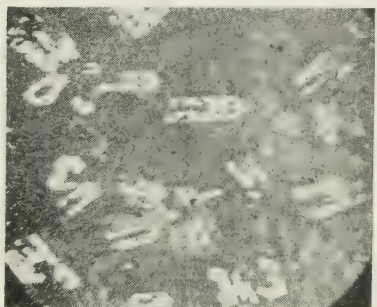


Fig. 18. Crystals.
5% Cu, f.c. × 20 diams. o.



Fig. 19. Crystals.
5% Cu, f.c. × 10 diams. o.

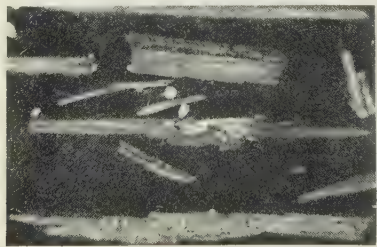


Fig. 20.
5% Cu, Cast. × 20 diams. v.

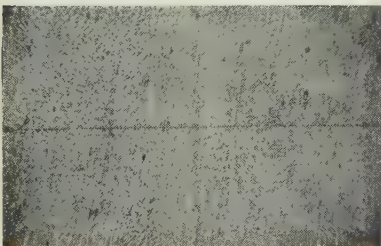
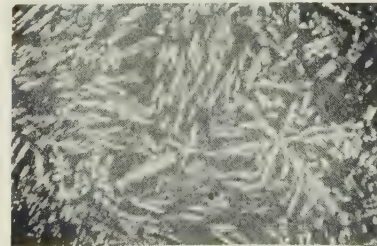


Fig. 21.
8% Cu. × 20 diams. v.



f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

Fig. 22.

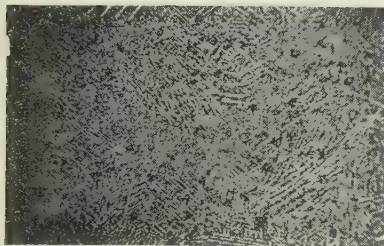
8% Cu, Cast. $\times 20$ diams. v.

Fig. 23.

10% Cu. $\times 20$ diams. v.

Fig. 24. Crystals.

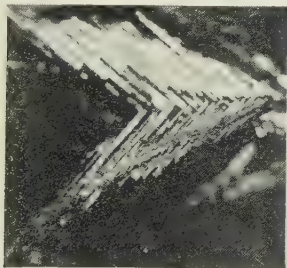
10% Cu, f.c. $\times 10$ diams. o.

Fig. 25.

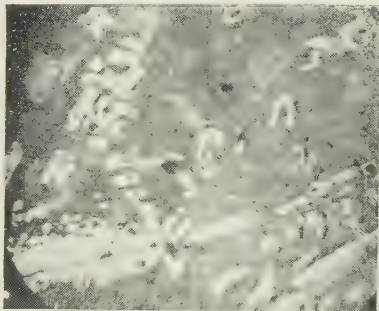
10% Cu, f.c. $\times 20$ diams. v.

Fig. 26.

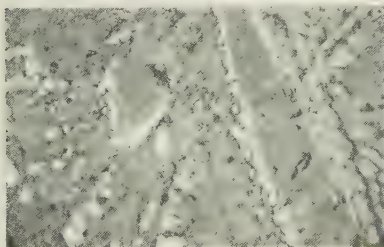
10% Cu, f.c. $\times 20$ diams. v.

Fig. 27.

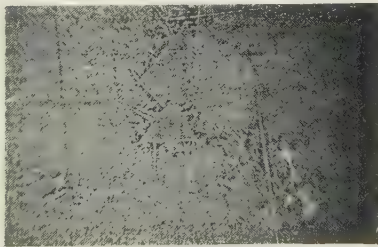
10% Cu, Cast. $\times 20$ diams. v.

Fig. 28.

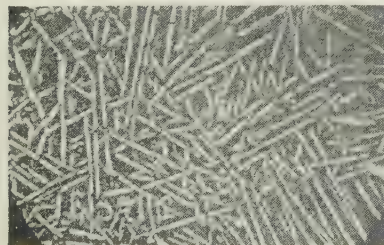
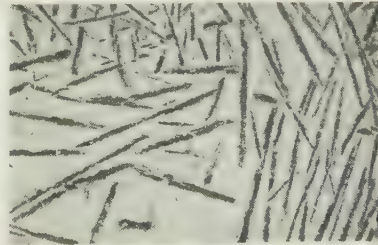
20% Cu. $\times 20$ diams. v.

Fig. 29.

20% Cu. $\times 20$ diams. o.

f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

Fig. 30.

20% Cu, f.c. × 20 diams. v.

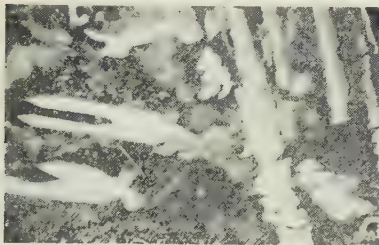


Fig. 31. Crystal.

20% Cu, f.c. × 20 diams. o.

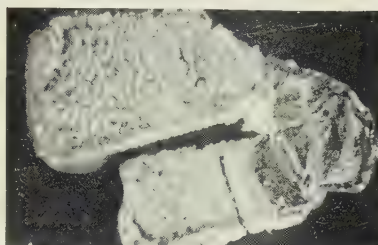


Fig. 32. Crystal.

20% Cu, f.c. × 10 diams. o.

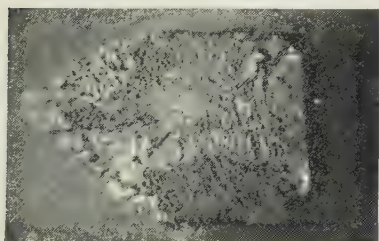


Fig. 33.

20% Cu, f.c. × 20 diams. v.



Fig. 34.

20% Cu, Cast. × 20 diams. v.

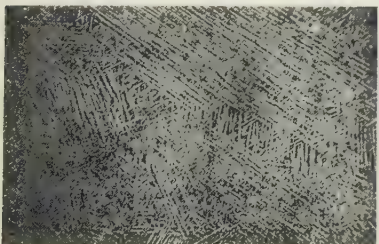


Fig. 35.

30% Cu. × 20 diams. v.

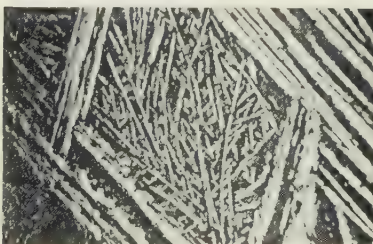


Fig. 36.

30% Cu, Cast. × 20 diams. v.

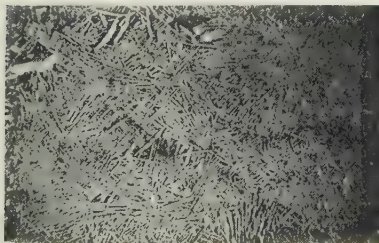
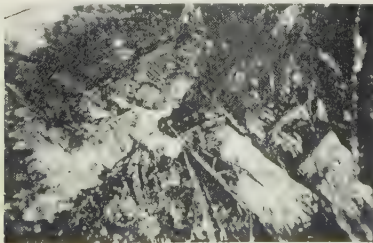


Fig. 37. Cast. Surface.

33% Cu. × 20 diams. v.



f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

Fig. 38.

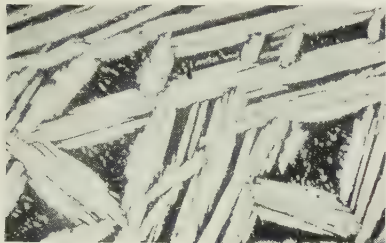
40% Cu. $\times 20$ diams. v.

Fig. 39.

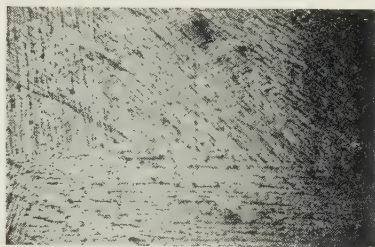
40% Cu, Cast. $\times 20$ diams. v.

Fig. 40. Cast. Surface.

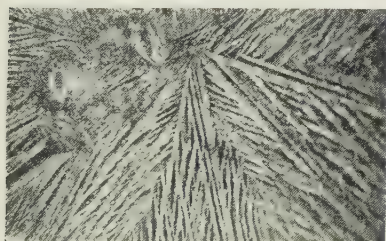
40% Cu. $\times 20$ diams. v.

Fig. 41.

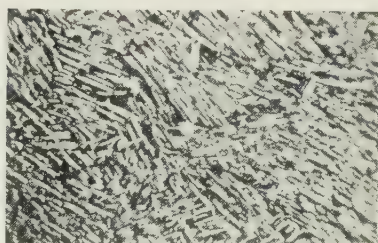
41% Cu. $\times 20$ diams. v.

Fig. 42.

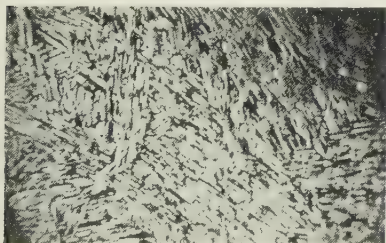
43% Cu. $\times 20$ diams. v.

Fig. 43.

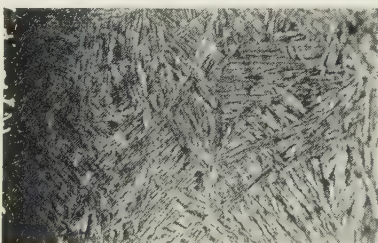
43% Cu, Cast. $\times 20$ diams. v.

Fig. 44. Cast. Surface.

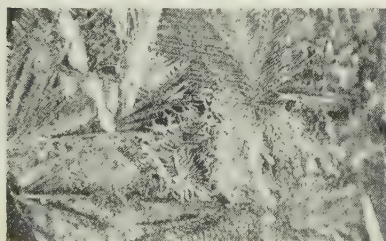
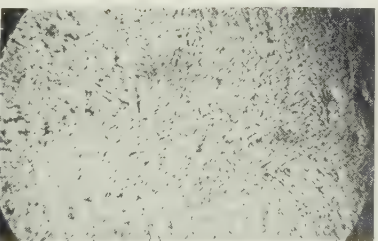
43% Cu. $\times 20$ diams. o.

Fig. 45.

46% Cu. $\times 20$ diams. v.

f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

Fig. 46.

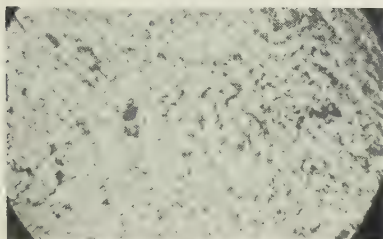
50% Cu. $\times 18$ diams. v.

Fig. 47.

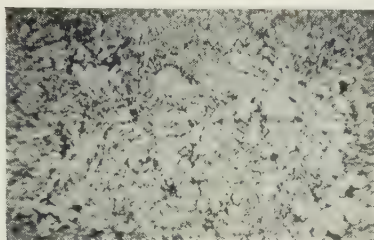
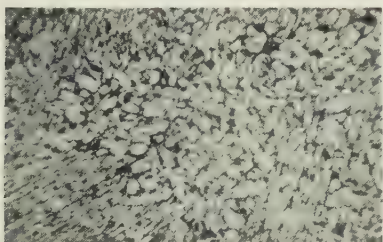
*Quenched below Break 1, Fig. 1.*50% Cu. $\times 20$ diams. v.Fig. 48. *Quenched below Break 2.*50% Cu. $\times 20$ diams. v.

Fig. 49.

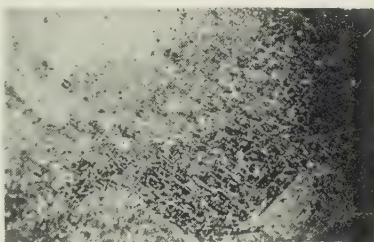
56% Cu. $\times 20$ diams. v.

Fig. 50.

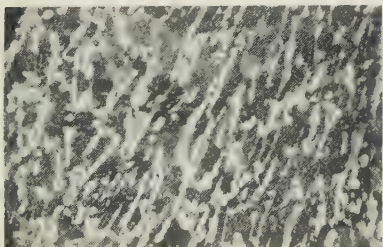
60% Cu, f.c. $\times 20$ diams. v.

Fig. 51.

61.5% Cu, f.c. $\times 20$ diams. o.

Fig. 52.

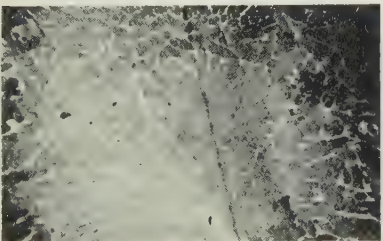
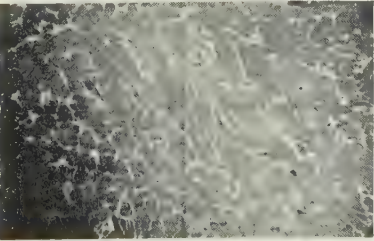
62.5% Cu, f.c. $\times 20$ diams. v.

Fig. 53.

63% Cu, f.c. $\times 20$ diams. o.

f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

Fig. 54.

64% Cu, f.c. × 20 diams. v.

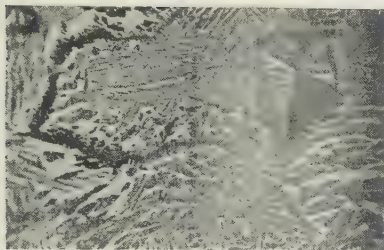


Fig. 55.

65% Cu, f.c. × 20 diams. v.

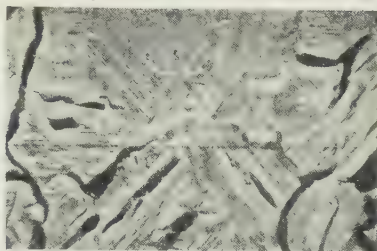


Fig. 56.

65% Cu, f.c. × 53 diams. v.

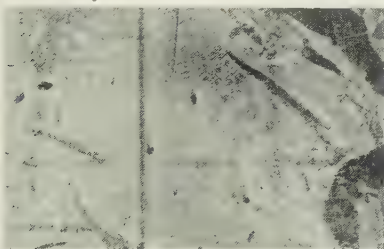


Fig. 57.

66% Cu, f.c. × 20 diams. v.

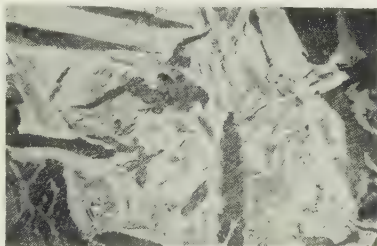


Fig. 58.

66% Cu. × 20 diams. v.

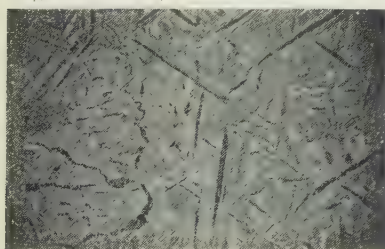


Fig. 59. Quenched on Break 1.

66% Cu. × 20 diams. v.

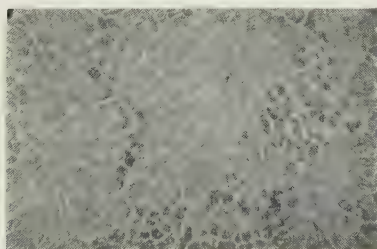


Fig. 60. Quenched on Solidification.

66% Cu. × 20 diams. v.

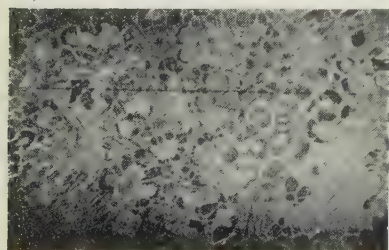
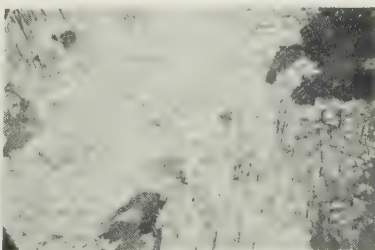


Fig. 61. Quenched below Break 1.

66% Cu. × 20 diams. v.



f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

Fig. 62.

66% Cu. Quenched below Break 2.



Fig. 63. Cast on plate.

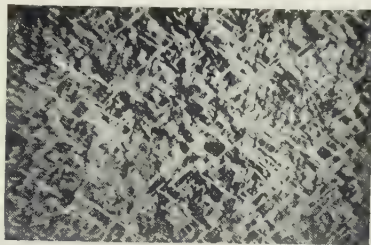
66% Cu, Surface Section $\times 20$ diams. v.

Fig. 64. Ingot.

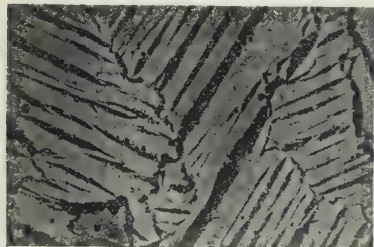
66% Cu. Surface Section. $\times 20$ diams. v.

Fig. 65.

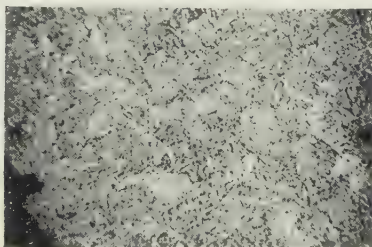
68.3% Cu, f.c. $\times 20$ diams. v.

Fig. 66. Cast on plate.

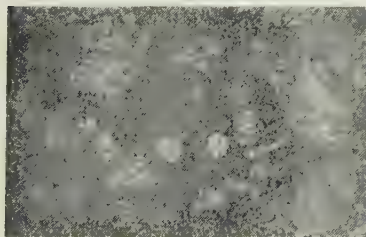
68.3% Cu. $\times 20$ diams. o.

Fig. 67. Ingot.

68.3% Cu. $\times 20$ diams. o.

Fig. 68. Quenched on Solidification.

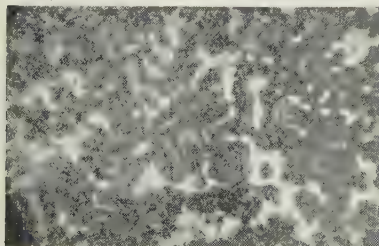
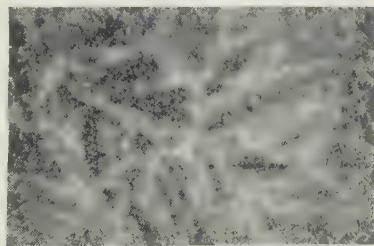
68.3% Cu. $\times 20$ diams. v.

Fig. 69. Quenched on Solidification.

68.3% Cu. $\times 33$ diams. v.

f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

Fig. 70.

72% Cu, f.c. × 20 diams v.

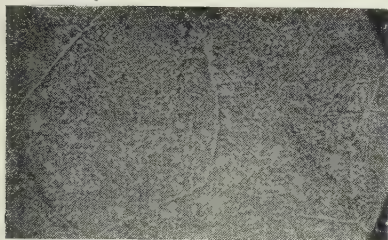


Fig. 71.

73% Cu, f.c. × 20 diams. v.

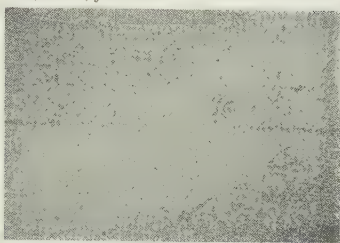


Fig. 72. Surface Section.

73% Cu. × 33 diams. v.

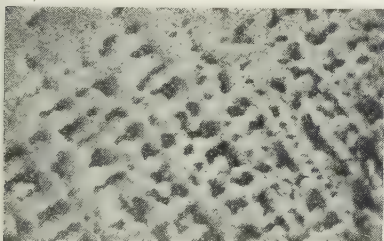


Fig. 73.

73% Cu. × 53 diams. v.

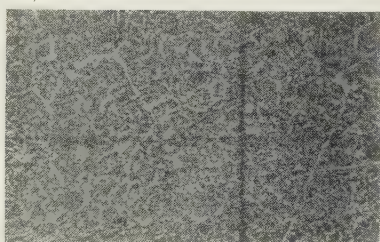


Fig. 74. Quenched on Solidification.

73% Cu. × 20 diams. v.

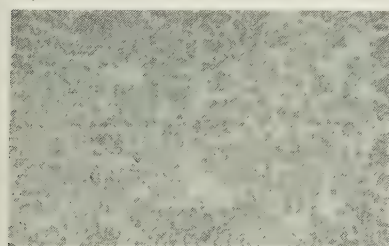


Fig. 75. Quenched at 650° C.

73% Cu. × 20 diams. v.

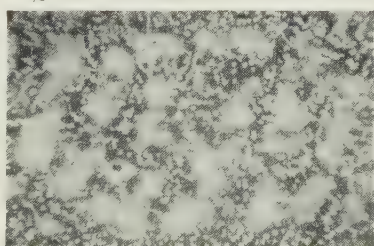


Fig. 76. Quenched at 500° C.

73% Cu.

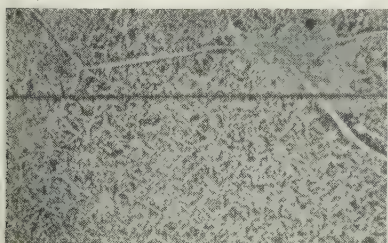
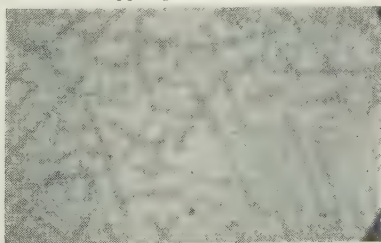


Fig. 77. Cast. Vertical Section.

73% Cu, Upper part. × 20 diams. v.



f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

Fig. 78.

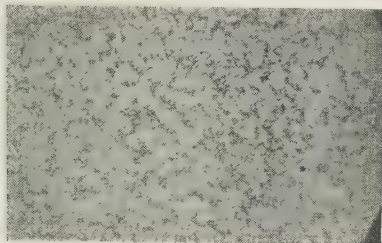
*Reheated, Quenched, and Annealed.*73% Cu, f.c. $\times 20$ diams. v.

Fig. 79.

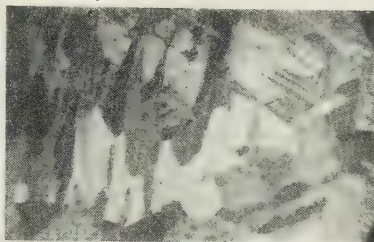
74% Cu, f.c. $\times 20$ diams. o.

Fig. 80.

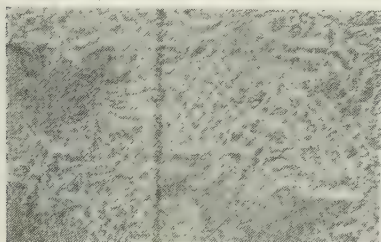
74% Cu, f.c. $\times 53$ diams. v.

Fig. 81. Cast Surface.

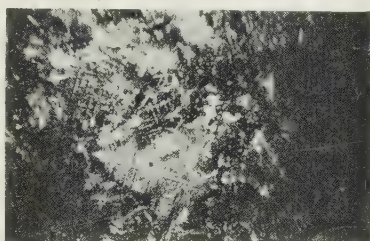
75% Cu, f.c. $\times 20$ diams. v.

Fig. 82. Cast. Surface Section.

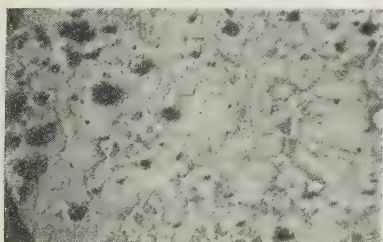
75% Cu. $\times 20$ diams. v.

Fig. 83. Reheated and Quenched.

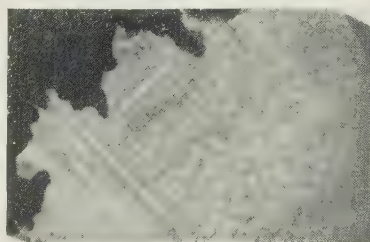
75% Cu, f.c. $\times 20$ diams. v.

Fig. 84.

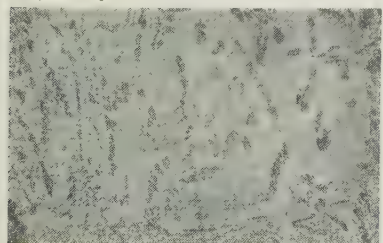
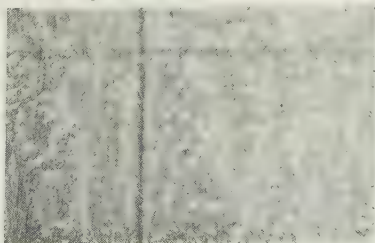
76% Cu, f.c. $\times 20$ diams. v.

Fig. 85.

76% Cu, f.c. $\times 53$ diams. o.

f.c. furnace-cooled. o. oblique illumination. v. vertical illumination.

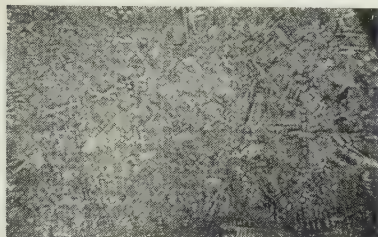
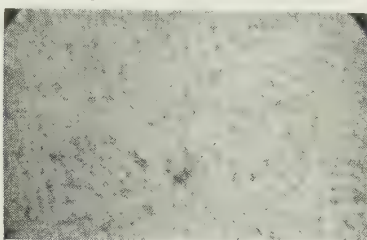
Fig. 86. *Quenched at Solidification.*76% Cu. $\times 20$ diams. *v.*Fig. 87. *Reheated and Quenched.*76% Cu, *f.c.* $\times 20$ diams. *v.*

Fig. 88.

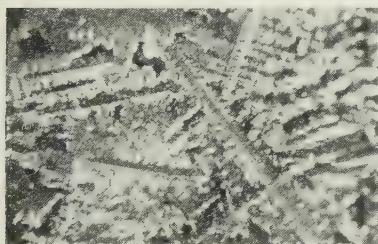
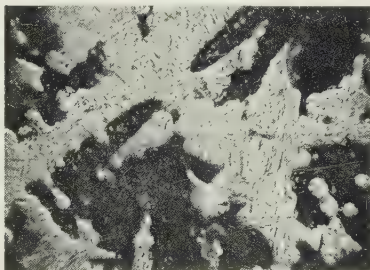
77% Cu, *f.c.* *Surface.* $\times 10$ diams. *o.*Fig. 89. *Surface Section.*77% Cu, *f.c.* $\times 20$ diams. *v.*

Fig. 90.

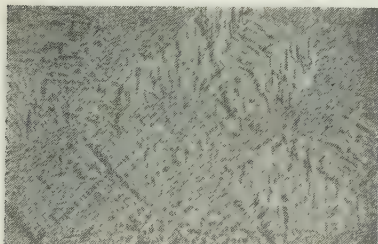
77% Cu. $\times 20$ diams. *o.*

Fig. 91.

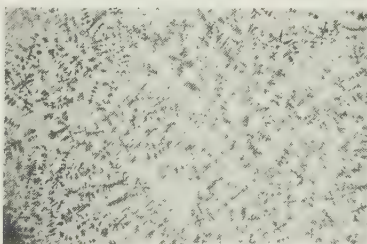
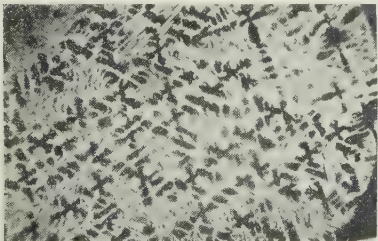
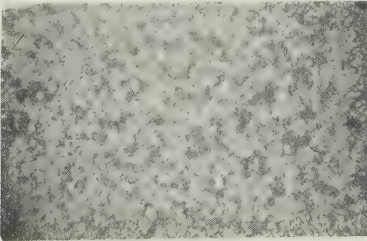
80% Cu. $\times 20$ diams. *v.*

Fig. 92.

80% Cu. $\times 20$ diams. *v.*Fig. 93. *Quenched Liquid.*80% Cu. $\times 20$ diams. *v.*

f.c. furnace-cooled. *o.* oblique illumination. *v.* vertical illumination.

Fig. 94.

*Quenched below Break 1.*80% Cu. $\times 20$ diams. v.

Fig. 95.

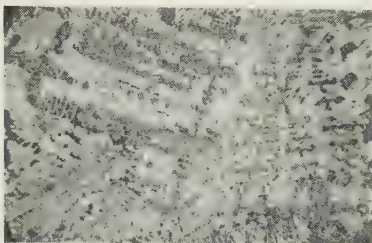
*Quenched below Break 2.*80% Cu. $\times 20$ diams. v.

Fig. 96.

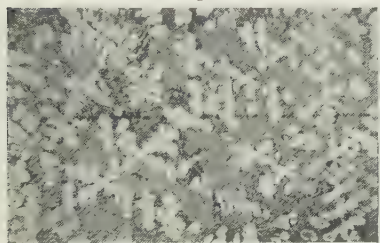
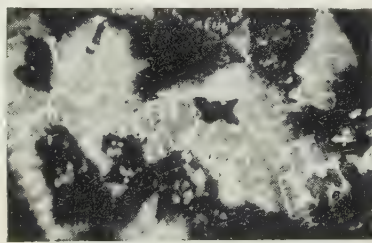
The same as Fig. 95. Centre.Fig. 97. *Surface Section.*80% Cu. $\times 20$ diams. v.

Fig. 98.

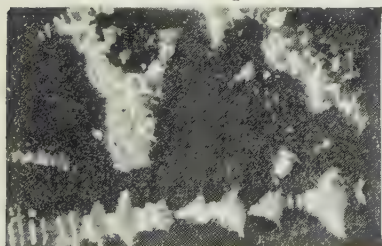
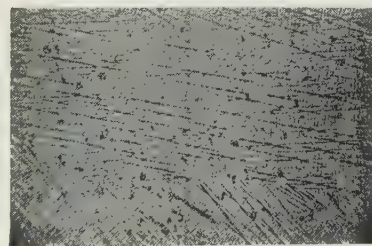
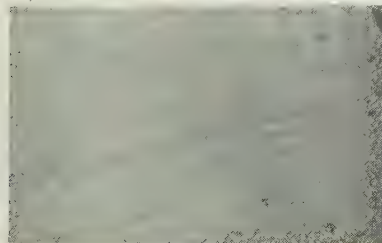
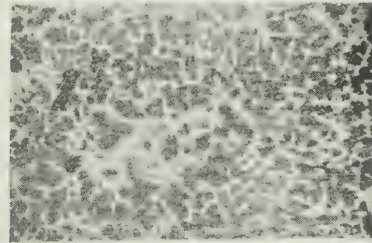
The same as Fig. 97.Fig. 99. *Cast. Vertical Section.*80% Cu. $\times 20$ diams. v.Fig. 100. *Cast and Annealed.*80% Cu. $\times 20$ diams. v.

Fig. 101.

85% Cu. $\times 20$ diams. v.

f.c. furnace-cooled. *o.* oblique illumination. *v.* vertical illumination.

Fig. 102.

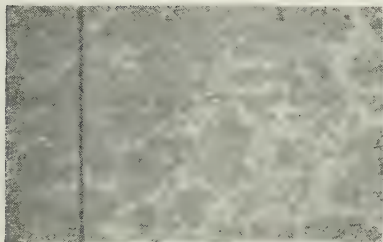
85% Cu. $\times 53$ diams. v.

Fig. 103.

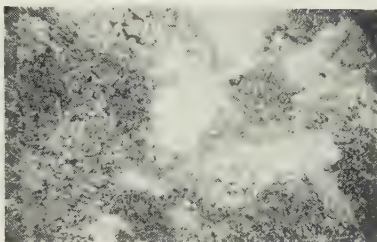
90% Cu. $\times 20$ diams. v.

Fig. 104. Surface Section.

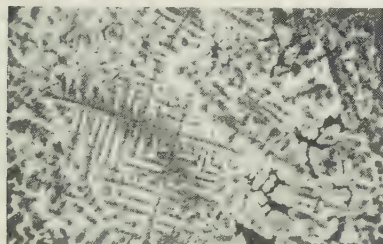
90% Cu. $\times 20$ diams. v.

Fig. 105.

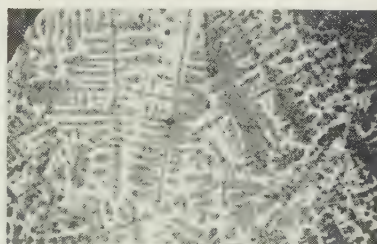
90% Cu. $\times 20$ diams. v.

Fig. 106.

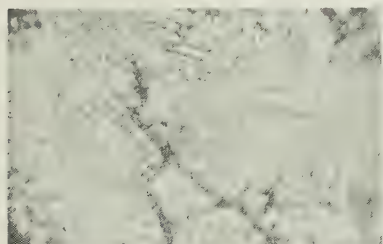
95% Cu. Surface. $\times 20$ diams. o.

Fig. 107.

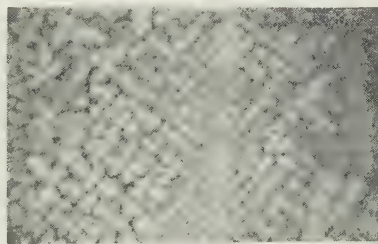
97.5% Cu. $\times 20$ diams. v.

Fig. 108. Top of Chilled Alloy.

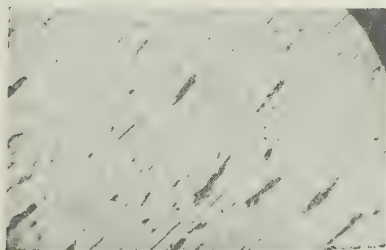
65% Cu, f.c. $\times 20$ diams. v.

Fig. 109.

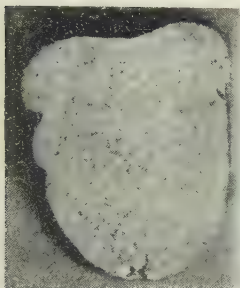
70-80% Cu, f.c. $\times 20$ diams. v.

f.c. furnace-cooled.

o. oblique illumination.

v. vertical illumination.

Fig. 111. 1% Cu, f.c.



COPPER-TIN ALLOYS.

Plate 203.

Fig. 112. 5% Cu, f.c.

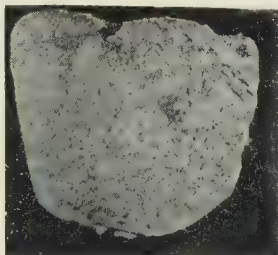


Fig. 113. 10% Cu, f.c.



Fig. 114. 20% Cu, f.c.



Fig. 115. 40% Cu.

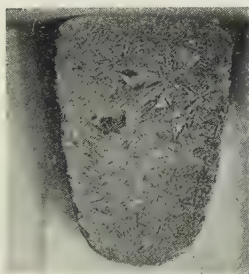


Fig. 116. 40% Cu, f.c.

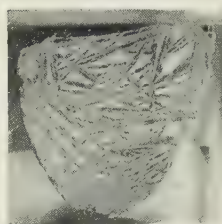


Fig. 117.
40% Cu. Horiz. Section.

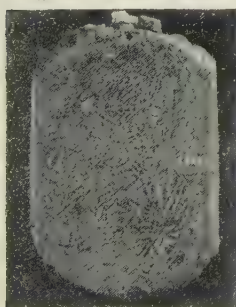


Fig. 118. 45% Cu, f.c.

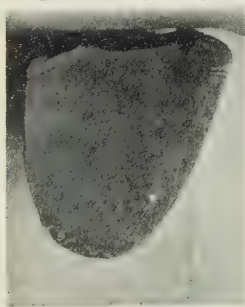


Fig. 119.
Beck Reflector,
and Sorby Mirror.



Fig. 121. Camera and Microscope.

Fig. 120.
Beck
Illuminator.



f.c. furnace-cooled.

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(Dr. T. K. Rose's remarks.)

Fig. 122. Crystals of $Sb Cu_3$.
83.33% Sn, 11.11% Sb, and 5.5% Cu.

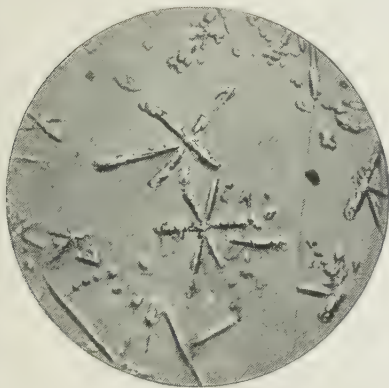
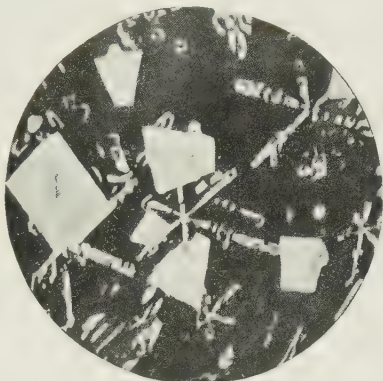


Fig. 123. The same, etched with HCl.
Stars of $Sn Cu_3$, Cubes $Sb Sn$.



(Mr. Bertram Blount's communication.)

Fig. 124. Pure Copper, Electrolytically deposited.
Long. Sectn. $\times 115$ diams.

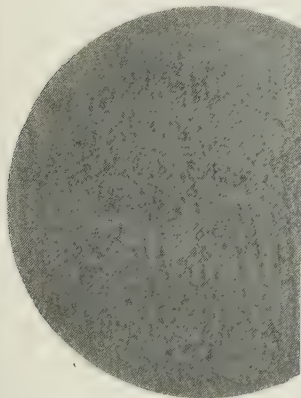
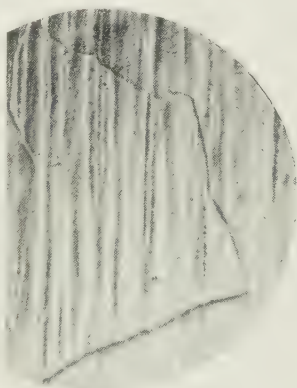


Fig. 125. The same, fused. $\times 40$ diams.



ANALYSIS.

Cu.	99.961
As.	Nil.
Sb.	0.002
Sn.	Nil.
Pb.	Nil.
Bi.	Nil.
Fe.	0.005
Ni.	Nil.
S.	Trace
O.	0.025

 99.993

Fig. 126. Commercial Copper.
Long. Sectn. $\times 115$ diams.

Commercial Copper.

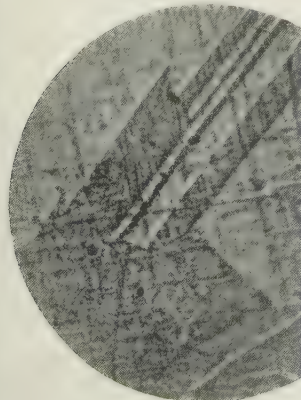
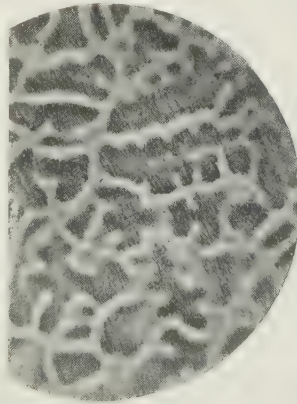


Fig. 127. The same, fused. $\times 40$ diams.



ANALYSIS.

Cu.	99.54
As.	0.12
Sb.	Trace
Pb.	0.17
Bi.	Trace
Fe.	Trace
Ni.	0.03
O.	0.15

 100.01

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Engineers 1901.

(Mr. J. T. Milton's remarks.)

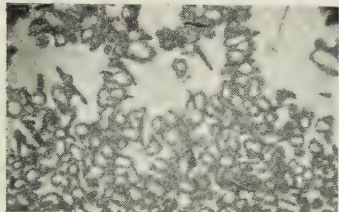
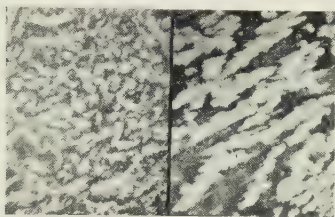
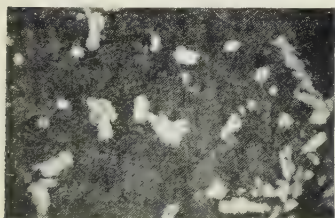
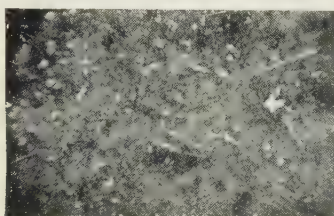
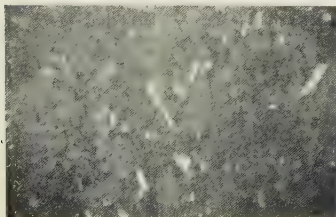
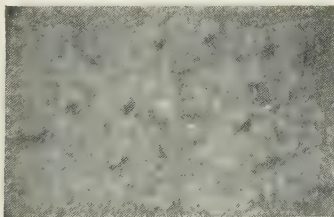
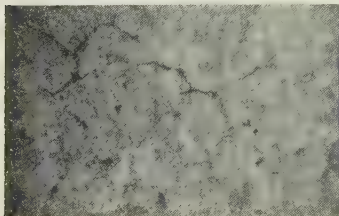
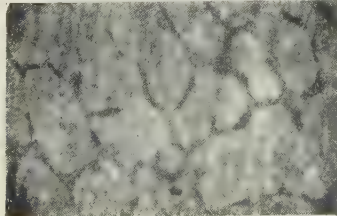
Fig. 128. *Slowly cooled.**White Metal.* $\times 40$ diams.

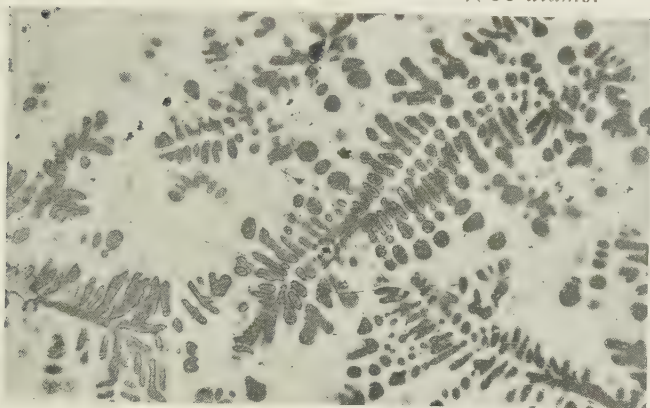
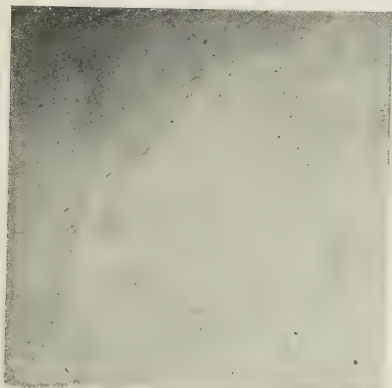
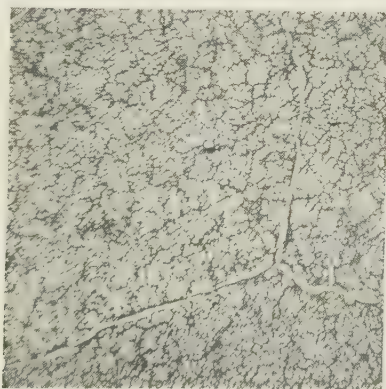
Fig. 129.

8.5% Cu. $\times 40$ diams.
Cast on chill. *Slowly cooled.*Fig. 130. *Slowly cooled.*4% Cu. $\times 40$ diams.Fig. 131. *Slowly cooled.*2% Cu. $\times 40$ diams.Fig. 132. *Slowly cooled.*1% Cu. $\times 40$ diams.Fig. 133. *Slowly cooled.*.5% Cu. $\times 40$ diams.Fig. 134. *Slowly cooled.*
25% Cu. $\times 40$ diams.Fig. 135. *Slowly cooled.*
Sn. Deeply etched. $\times 40$ diams.

(Appendix to Messrs Heycock and Neville's remarks.)

Fig. 137.

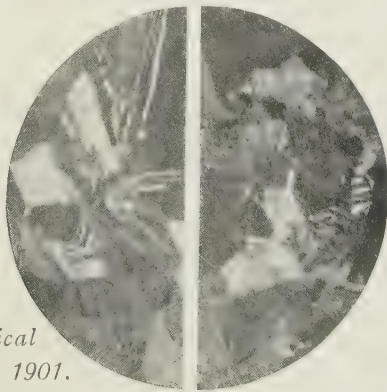
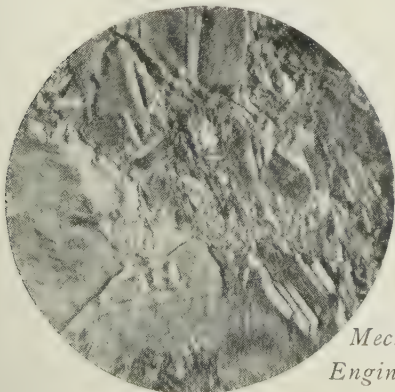
30% Sn. Chilled at 740° C. × 50 diams.

Fig 138. Chilled at 630° C.
30% Sn. × 50 diams.Fig. 139. Chilled at 500° C.
30% Sn. × 50 diams.

(Author's reply.)

Electro-copper direct from Vats. Etched by HNO_3 .

99.9% Cu. Fig. 141. × 33 diams. v. 99.9% Cu. Fig. 142. × 33. v.

*Mechanical
Engineers 1901.*

WILLIAM CAMPBELL, entered the University of Durham College of Science, England, in October, 1895, with a Yorkshire County Council scholarship. In September, 1896, was made a corporation exhibitor. In June, 1897, obtained the title of A. Sc., and the following year the degree of B. Sc. [honors]. During 1898-9 acted as instructor in metallurgy and lecturer in geology. In June, 1899, the Royal Commissioners for the exhibition of 1851 awarded him a scholarship for scientific research. Entered the Royal School of Mines, London, October of the same year. Scholarship renewed for a second year to continue research under Sir William Roberts-Austen, and renewed for an exceptional third year to work under Prof. H. M. Howe at Columbia University. October, 1901, Post-graduate work in metallurgy. Carnegie scholar of Iron and Steel Institute, May, 1902; University Fellow in Metallurgy, June, 1902; M. Sc. Durham University, June, 1903.

PUBLISHED PAPERS:—

Crystalization produced in Solid Metal by pressure.

Metallographist, V. 157.

The Alloys of Copper and Tin,

Brass Founder and Finisher, May, June and July, 1902.

On the Structure of Metals and Binary Alloys,

Journal Franklin Inst., July-Sept., 1902.

[With J. A. Mathews]: Alloys of Aluminum,

Journal American Chem. Soc. Vol. XXIV, -3-253.

